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# Reactor Test Project for Chemical Removal of Pyritic Sulfur from Coal; Volume I. Final Report

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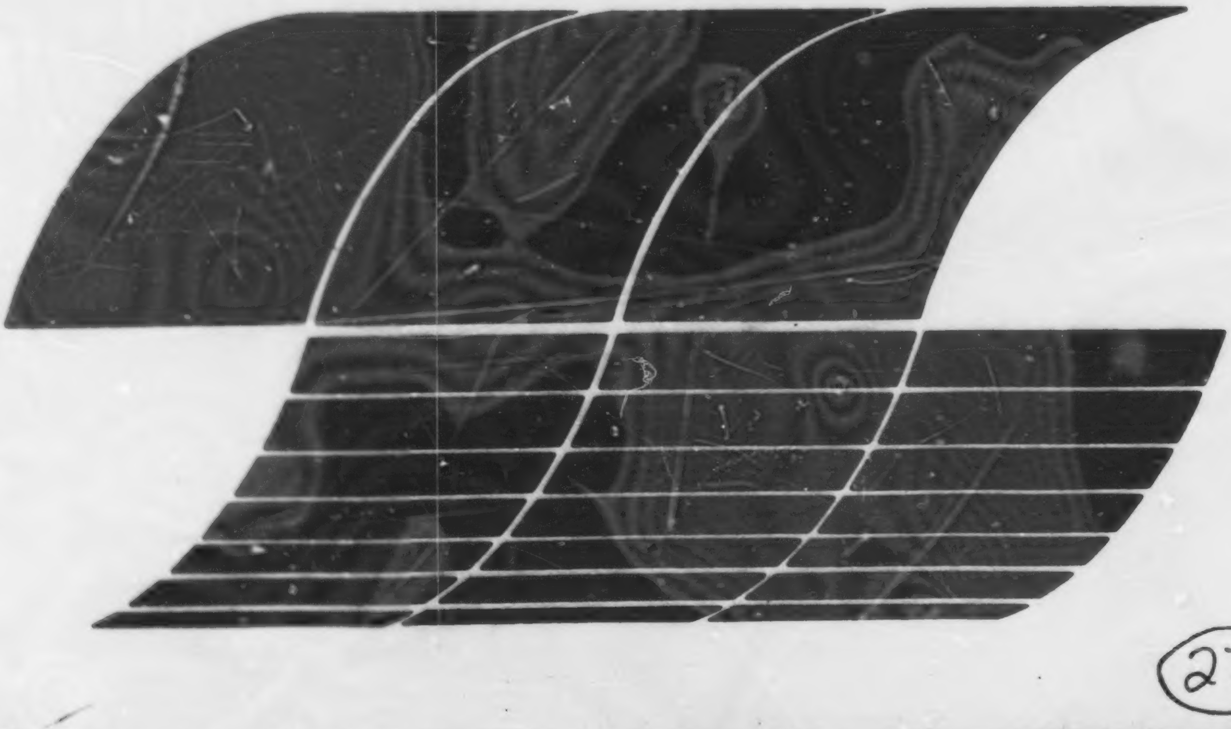

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EPA-600/7-79-013a

January 1979

# Reactor Test Project for Chemical Removal of Pyritic Sulfur from Coal;
## Volume I. Final Report

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# ABSTRACT

Plant checkout and shakedown was completed at the end of September and initial plant process performance was evaluated on an Appalachian coal. Operation of the plant through January of 1978 demonstrated that the Reactor Test Unit (RTU) could be run continuously in three-shift operation to reduce the coal from 2.4 lbs $SO_2/10^6$ Btu to a level of 1.0 to 1.2 lbs $SO_2/10^6$ Btu, after rinsing and extraction of generated elemental sulfur. There was no measurable coal oxidation during processing and leach rates in the plant were greatly improved over bench-scale values. The leach solution/coal/oxygen environment was found to be corrosive to the installed stainless steel reactor, necessitating future upgrading to support additional testing. Bench-scale experimentation showed that the leach solution can be used as a homogeneous dense-media to efficiently gravity-separate coal prior to processing. Beneficial engineering cost improvements are obtained based on using this approach, resulting in capital cost estimates of \$68-\$69/KW and with \$0.44-\$0.50/$10^6$ Btu processing costs, including amortization of capital, for input coal costing \$0.78-\$0.81/$10^6$ Btu. Overall energy efficiency was 93 to 96 percent.

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Gratitude is due to the American Electric Power Service Corporation for providing 300 tons of coal for this initial operation phase of the plant and most particularly to Sam Ruggeri of that organization.

## METRIC CONVERSION FACTORS

In compliance with EPA policy, metric units have been used extensively in this report (followed by British units in parentheses). However, in some cases, British units have been used for ease of comprehension. For these cases, the following conversion table is provided:

| British | Metric |
|---|---|
| 1 Btu | 252 calories |
| 1 Btu | $2.93 \times 10^{-4}$ kilowatt-hours |
| 1 kw | 1,000 joules/sec |
| 1 hp (electric) | 746 joules/sec |
| 1 psi | 0.07 kilograms/$cm^2$ |
| 5/9 (°F-32) | °C |
| 1 inch | 2.54 centimeters |
| 1 ft | 0.3048 meter |
| 1 $ft^2$ | 0.0929 $meters^2$ |
| 1 $ft^3$ | 0.0283 $meters^3$ or 28.3 liters |
| 1 gallon | 3.79 liters |
| 1 pound | 0.4536 kilograms |
| 1 ton (short) | 0.9072 metric tons |

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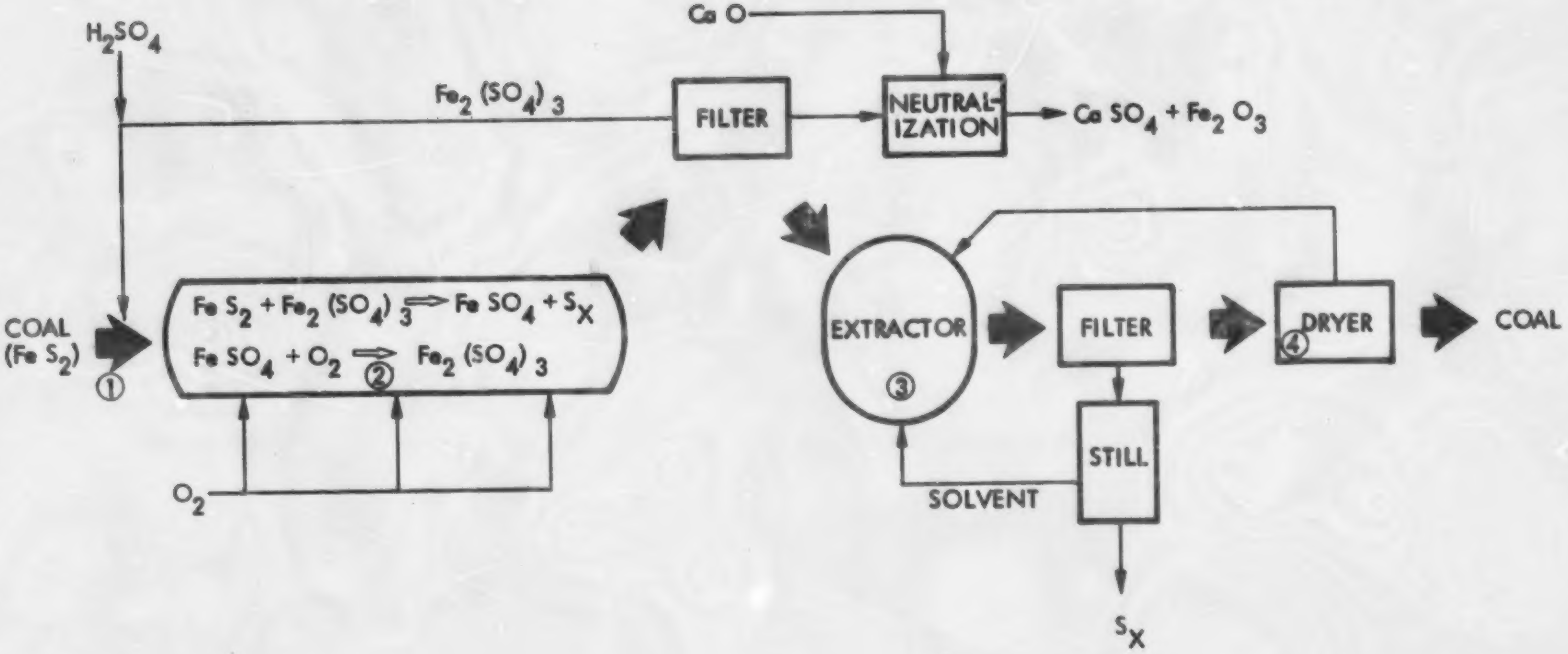
# 1. INTRODUCTION

The Meyers Process is a technology for chemically removing essentially all of the pyritic sulfur from coal through a mild oxidative treatment. Important pollutant trace elements of lead, cadmium, and arsenic are removed at the same time. It is particularly cost effective for providing compliance coal for industrial boilers and smaller electric utilities, and for recovering and desulfurizing waste fine coal rejected from mining and washing operations.

A process schematic is shown in Figure 1. Coal is mixed with an aqueous solution of ferric sulfate (Step 1), previously derived from the coal, to form a slurry. The slurry is raised in temperature to $100^{o}$-$130^{o}$C (Step 2) where the ferric sulfate oxidizes the pyritic sulfur content of the coal to form elemental sulfur and additional iron sulfate. At the same time oxygen or air is introduced to regenerate the reacted ferric sulfate. Iron sulfate dissolves into the leach solution while the elemental sulfur is removed in a second extraction (Step 3). The coal is dried and solvent recovered (Step 4). The products of the process are iron sulfate, which may be limed to give a dry gypsum and iron oxide material and elemental sulfur. Trace elements from the coal are rejected from the leach solution with the stabilized gypsum-iron oxide solid. Elemental sulfur is the most desirable product which can be obtained in the process of controlling sulfur oxide pollution since it may be easily stored without additional pollution or may be marketed. The gypsum-iron oxide product is a safe and storable solid product.

After testing the process on some 40 U.S. coals(1,2,3) and performing 200 fully material balanced bench-scale extractions,(4,5) the value of the process for controlling the sulfur content of coal was firmly established and the data necessary for design of a test plant was then available. Engineering design background obtained through extensive studies at both TRW(4,5,6) and various engineering organizations(7,8) provided confidence that the process

2



Ca O
$H_2SO_4$
$Fe_2(SO_4)_3$
FILTER
NEUTRALIZATION
$CaSO_4 + Fe_2O_3$
COAL
$(FeS_2)$
①
$FeS_2 + Fe_2(SO_4)_3 \Rightarrow FeSO_4 + S_X$
$FeSO_4 + O_2 \Rightarrow Fe_2(SO_4)_3$
②
$O_2$
EXTRACTOR
③
FILTER
DRYER
④
COAL
STILL
SOLVENT
$S_X$

Figure 1. Meyers Process

was economically attractive and indicated important engineering data which could only be obtained at test plant scale.

It was determined that the initial test plant evaluation should concentrate on the key process steps of coal-leach solution slurry formation, leaching, regeneration and filtration. A test plant, termed the Reactor Test Unit, was constructed at TRW's San Juan Capistrano site for the purpose of testing these portions of the process (Figure 2). The plant, sized to process from 1/8 to 1/3 ton/hour of coal was dedicated in April, 1977.

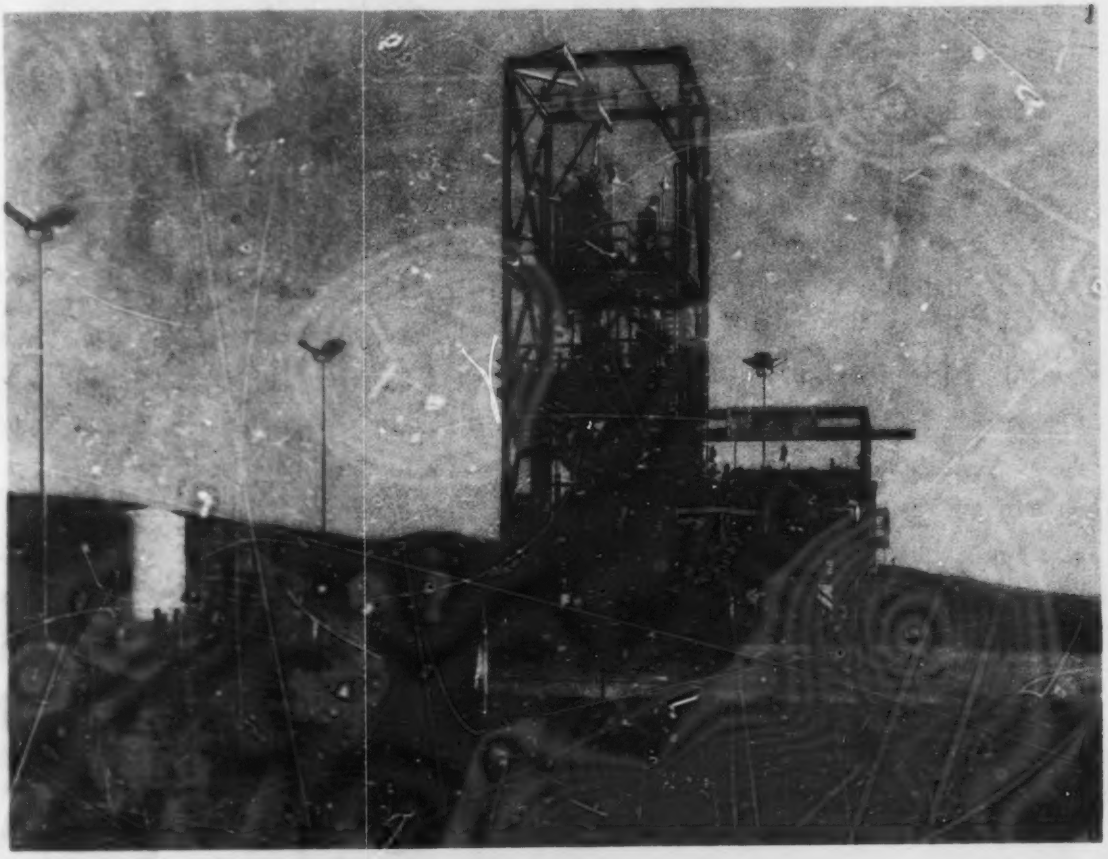


Figure 2. Reactor Test Unit

Plant checkout and shakedown was completed at the end of September and initial process performance was evaluated on coal donated by the American Electric Power Service Corporation (AEP) from its Martinka mine (Appalachian coal). Operation of the plant through January of 1978 demonstrated that the Reactor Test Unit (RTU) could be run continuously in three-shift operation to reduce the AEP coal from 2.4 lbs $SO_2/10^6$ Btu to a level of 1.0-1.2 lbs $SO_2/10^6$ Btu, after rinsing and extraction of generated elemental sulfur. The coal product is shown as a cake on the plant belt-filter in Figure 3. There was no measurable coal oxidation. Leach rates in the RTU were greatly improved over bench-scale values, allowing elimination of the use of a second process reactor for completing pyrite removal. The leach solution/coal/oxygen environment was found to be corrosive in the installed stainless steel reactor, necessitating future upgrading of the reactor material of construction to support additional testing.

Supporting bench-scale experimentation showed that the iron sulfate-sulfuric acid leach solution can be used as a homogeneous dense media to efficiently gravity-separate fine coal at specific gravities of 1.2 to 1.35. Beneficial engineering cost improvements are obtained, based on using this gravity-separation effect, whereby a significant portion of the input coal which floats in the leach solution and is almost pyrite free, may bypass the reactor, elemental sulfur extraction and dryer portions of the Meyers Process (Figure 4). This revised technology is termed the Gravichem Process. When applied, at bench-scale, to a Tennessee Valley Authority (Interior Basin) coal containing 12% ash and 7 lbs of $SO_2/10^6$ Btu, two products are obtained, a 4% ash float coal containing 3 lbs $SO_2/10^6$ Btu and an 11-12% ash sink coal containing 4 lbs $SO_2/10^6$ Btu after treatment by the Meyers Process. Both of these products meets State $SO_x$ emission standards for this coal. Because of these promising results, TVA has shipped 300 tons of coal to TRW to demonstrate desulfurization in the RTU.

Laboratory experimentation also showed that the solvent system, acetone and water, is the most economically attractive method thus far investigated for removal of generated elemental sulfur from treated coal.

Process cost forecasts based on both RTU data and supporting laboratory experimentation for the Gravichem Process are $68-69/KW capital cost with

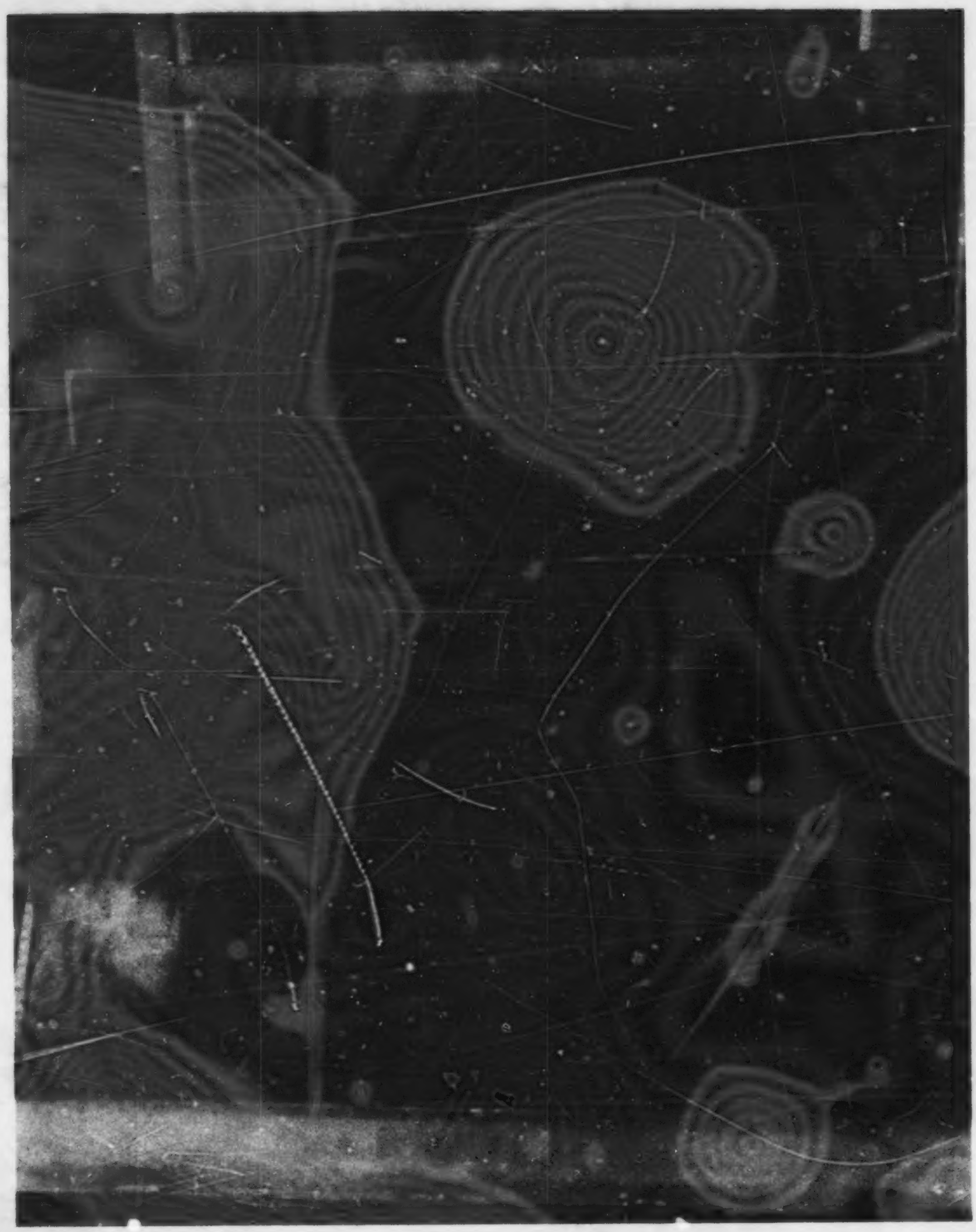


Figure 3. Reacted Coal on Belt Filter

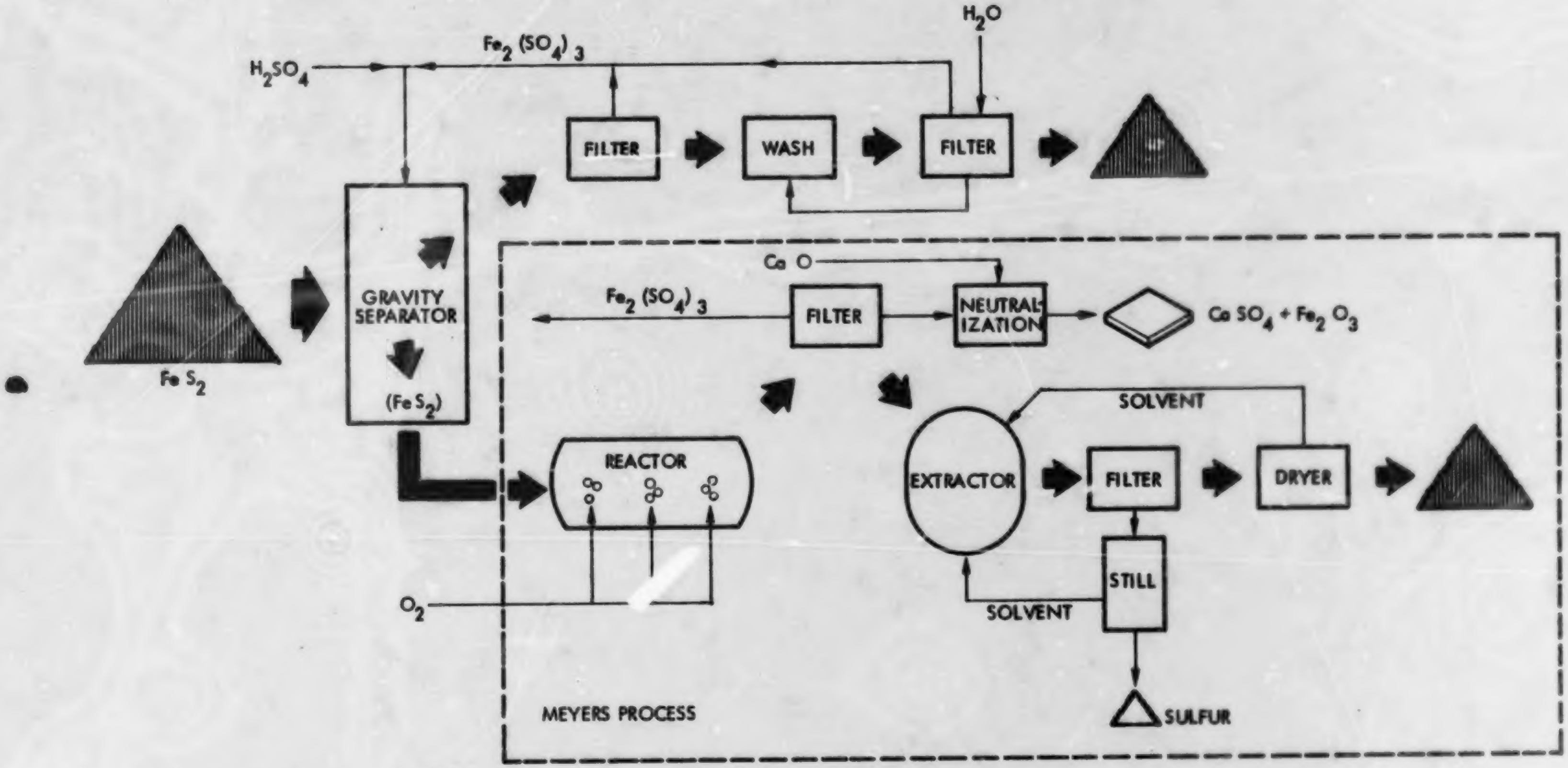

$H_2O$
$H_2SO_4$
$Fe_2(SO_4)_3$
FILTER
WASH
FILTER
GRAVITY SEPARATOR
(FeS$_2$)
FeS$_2$
Ca O
$Fe_2(SO_4)_3$
FILTER
NEUTRALIZATION
$CaSO_4 + Fe_2O_3$
SOLVENT
REACTOR
EXTRACTOR
FILTER
DRYER
STILL
SOLVENT
$O_2$
MEYERS PROCESS
SULFUR

Figure 4. Gravichem Process

\$0.44-0.50 $10^6$/Btu, processing costs, including utility financed capital amortization, for input coal costing \$0.78-0.81/$10^6$/Btu. Overall energy efficiency for these process designs including both coal use for process heat and electric energy for plant operation is 93% to 96%.

The report is organized into nine sections to follow. Sections 2 and 3 present the conclusions and recommendations, respectively, which resulted in this study. The RTU is described in Section 4 and the operation of the plant in Section 5. A complete set of RTU data together with analysis of the data is presented in Section 6. The supporting bench-scale laboratory results are found in Section 7 and engineering design and full-scale process cost estimation in Section 8. A plan for vendor testing of process unit operations, not built into the RTU, is described in Section 9 and a detailed plant materials evaluation is presented in Section 10. The referenced appendices are continued in Volume II of this report.

# 2. CONCLUSIONS

## PLANT OPERATION RESULTS

1. The Reactor Test Unit (RTU) can be operated continuously for testing of Meyers Process units for coal-leach solution mixing, simultaneous coal leaching and leach solution regeneration, filtration of leach solution from treated coal and water washing of coal on the filter.

2. The input coal from American Electric Power Service Corporation's Martinka mine in Fairmont, West Virginia, containing 1% inorganic sulfur can be reliably and continuously reduced, in the RTU, to a pyritic sulfur level of 0.16% without any measurable coal loss and with coal heat content increases averaging 350 Btu/lb.

3. RTU coal product, after bench-scale extraction of residual sulfate and elemental sulfur, was continuously and reliably reduced to a total sulfur content of 0.68-0.75% and 1.0-1.2 lbs $SO_2/10^6$ Btu.

4. Leach rates in the RTU were improved over bench-scale values by an average factor of five due mainly to favorable coal segregation in the primary reactor.

5. Plant leacher-regenerator operation at temperatures ranging from 230°-270°F (110°-132°C), pressures of 30-80 psig and residence time of 5-8 hours was demonstrated.

6. The use of a single reactor-regenerator is sufficient to meet design basis pyrite removal and provide regenerated leach solution. The use of a secondary reactor to complete the reaction of pyrite with leach solution, found to be necessary at bench-scale, was demonstrated to be unnecessary in the Reactor Test Unit.

7. The leach solution/coal/oxygen environment caused corrosion in the primary reactor-regenerator system indicating that upgrading of the 316L material of construction for improved corrosion resistance is needed to support further testing.

8. The following materials were found to be suitable for leach solution-coal service at temperatures up to 90°C: fiber reinforced plastics, elastomers and 316L stainless steel. The

following materials were determined to be suitable for service at reactor-regenerator temperatures: up to 130°C, titanium, Hastaloy, and rubber-lined brick over mild steel.

9. No significant corrosion was observed in the leach solution-coal mix tank, flash-down tank, storage tanks or reactor-regenerator pumps.

## SUPPORTING EXPERIMENTATION RESULTS

10. The iron sulfate-sulfuric acid leach solution can be used as a homogenous liquid to efficiently gravity-separate fine coal from pyrite rich coal at specific gravities of 1.2 to 1.35.

11. Beneficial engineering cost improvements are obtained by using this gravity-separation effect to bypass a significant portion of the input coal around the reactor, elemental sulfur extraction and dryer units of the Meyers Process. This revised process is termed the Gravichem Process.

12. The Gravichem Process provides two products with no coal reject, a float coal containing 2-4% ash with almost no pyritic sulfur and a sink coal generally lower in ash than the input coal and also nearly pyrite-free after treatment by the Meyers Process. The two products can be used separately or combined.

13. Bench-scale testing of the Gravichem Process on the American Electric Power Service Corporation (Appalachian) coal gave two products: a float coal containing 1.0 lbs $SO_2/10^6$ Btu and a sink coal containing 1.1 lbs $SO_2/10^6$ Btu after treatment by the Meyers Process. Both products met New Source Performance Standards.

14. Bench-scale testing of the Gravichem Process on a Tennessee Valley Authority (Eastern Interior Basin) coal containing 12% ash and 7 lbs of $SO_2/10^6$ Btu gave two products: a 4% ash float coal containing 3 lbs $SO_2/10^6$ Btu and an 11-12% ash sink coal containing 4 lbs $SO_2/10^6$ Btu after treatment by the Meyers Process.

15. The solvent system, acetone and water, is the most economically attractive method thus far investigated for removal of generated elemental sulfur from treated coal. This solvent also dissolves and removes residual iron sulfate.

## ENGINEERING DESIGN RESULTS

16. Process cost forecasts for the Gravichem Process are \$68-69/KW capital cost with \$0.44-0.50/$10^6$ Btu, processing costs including utility financed capital amortization, for input coal costing \$0.78-0.81/$10^6$ Btu.

17. Coal energy efficiency is 94-97% for the Gravichem Process including coal use for process heating.

18. Overall energy efficiency including both coal use and electric energy for plant operation is 93-96%.

## 3. RECOMMENDATIONS

1. Design and replace the corroded primary reactor with an improved vessel constructed of either titanium or rubber-lined brick over mild steel.
2. Construct and test in integrated operation, a leach-solution gravity-separator unit to evaluate Gravichem separation and Meyers Process treatment of sink coal.
3. Test the operation of the plant on a coal from the Eastern Interior region of the United States, such as the Tennessee Valley Authority coal, 300 tons of which is now on hand.
4. Construct and test in integrated operation, Meyers Process units for continuous residual sulfate extraction, generated elemental sulfur extraction, coal drying, recovery of solvent, water and elemental sulfur by distillation and liming out of generated iron sulfate.

# 4. REACTOR TEST UNIT

During the past seven years, TRW has been involved in various stages of development of the Meyers Coal Desulfurization Process. The early work involved laboratory and bench scale testing(1,2,3,4,5) which was aimed at obtaining process application information and process design data. Those early efforts led to the design of the Reactor Test Unit (RTU). The design of the RTU was carried out in two steps; first a preliminary design to evaluate the overall approach and probable cost of the envisioned unit (6) and secondly, a detailed engineering and design effort which immediately preceded equipment procurement and RTU construction. The detailed engineering, procurement, and construction of the RTU occurred over a 19-month period. Immediately following plant construction, TRW initiated operator training, safety check-out, procedure verification, and RTU shake-down in May 1977.

This Section presents a detailed description of the RTU as constructed. Intended uses and capabilities of the integrated RTU are discussed as are those of each major unit operation sub-system in Section 4.1. Section 4.2 details the specific equipment which is incorporated into the RTU. Information such as equipment type, manufacturer, size, model, configuration, capacity, operating limits, and materials of construction is presented.

## 4.1 PROCESS DESCRIPTION

The Reactor Test Unit is a pilot scale coal processing facility designed to demonstrate those unit operations comprising the front end of the Meyers Process, namely, coal-reagent mixing, primary pyrite reaction and reagent regeneration, secondary (finishing) pyrite reaction and slurry filtration. Designed for high flexibility, the RTU has the capability of processing a range of suspendable coals up to approximately 8 mesh top-size and coarse coals up to approximately 3/8-inch top-size. Spent reagent may be regenerated either exclusive of, or simultaneously with, coal leaching. The primary reactor may be used as either a five-stage or a three-stage reaction unit to increase the available range of coal processing times.

The most common modes of RTU operation are represented schematically in Figure 5. Fine coal ground to the desired size is loaded into feed tank T-1. Dry coal is fed continuously by a live bottom feeder A-2 to the weigh belt A-3 which discharges through rotary valve A-4 to the three-stage mixer T-2 (stream 1). Aqueous iron sulfate leach solution (stream 2) enters T-2 after preheating in a heat exchanger E-2 and passing through the foam scrubber T-3. Steam is added (stream 3) to raise the slurry to its boiling point. Foaming, which may occur during the early stages of mixing, ceases when coal particle wetting is complete. The heated slurry (stream 4) is then pumped to a five-stage pressure vessel R-1 in which most of the pyrite is removed. R-1 Slurry heating is achieved by direct injection of steam into any or all reaction stages. Reagent regeneration may be carried out simultaneously with pyrite leaching by means of oxygen injection into any or all reaction stages (stream 5). Unusued oxygen saturated with steam (stream 6) is contacted in a foam knock out drum V-1 with the feed reagent (stream 7) to preheat the reagent and cool vent gases. Slurry in any stage of R-1 may be cooled by means of a cooling water heat exchanger E-1 which may be applied to slurry recirculation loops for removal of excess heat of reaction. Vent gas from both T-3 and V-1 are water scrubbed in T-4 to remove any traces of acid mist.

Reacted coal slurry (stream 8), at elevated temperature and pressure, is flashed into a flash drum T-5 for gas-liquid separation. Generated steam (stream 9) is condensed in T-4, and the condensate plus any entrained acid mist is removed with scrubber water. Reacted slurry (stream 10) is fed to the belt filter S-1. The filtrate, which is regenerated leach solution, is removed from the coal slurry through the evacuated filtrate receiver V-2 and pumped (stream 12) to the leach solution storage tank T-7. Coal on the filter belt is washed with water (stream 11) and discharged to coal storage. Wash water is removed through the evacuated wash water receiver V-3 and pumped (stream 13) to the liquid waste holding tank T-9 for subsequent disposal.

As a processing alternate, partially processed slurry from T-5 may be loaded into the secondary reactor R-2 for final depyritization in a batch mode. Slurry may be retained, heated and agitated, for extended periods of time in R-2 prior to being pumpted to S-1.

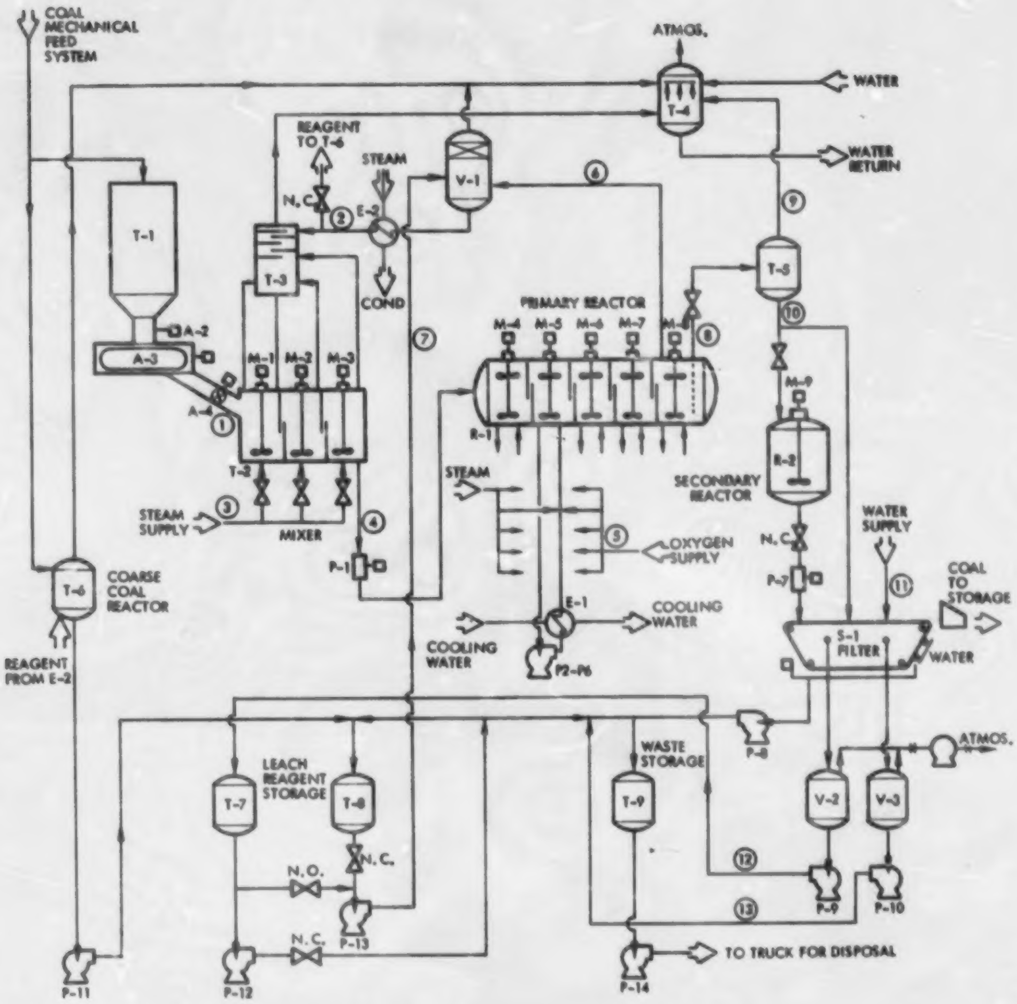

COAL MECHANICAL FEED SYSTEM
ATMOS.
WATER
T-4
WATER RETURN
REAGENT TO T-6
STEAM
N. C.
②
E-2
V-1
⑥
⑨
T-1
T-3
COND
T-5
PRIMARY REACTOR
M-4
M-5
M-6
M-7
M-8
⑧
⑩
A-2
A-3
M-1
M-2
M-3
⑦
M-9
A-4
①
R-1
R-2
T-2
STEAM
SECONDARY REACTOR
STEAM SUPPLY
③
MIXER
④
⑤
OXYGEN SUPPLY
N. C.
WATER SUPPLY
P-1
P-7
COAL TO STORAGE
T-6
COARSE COAL REACTOR
⑪
E-1
COOLING WATER
COOLING WATER
S-1 FILTER
WATER
P2-P6
REAGENT FROM E-2
P-8
ATMOS.
LEACH REAGENT STORAGE
WASTE STORAGE
T-7
T-8
T-9
V-2
V-3
N. C.
N. O.
⑫
⑬
P-9
P-10
P-13
N. C.
TO TRUCK FOR DISPOSAL
P-11
P-12
P-14

Figure 5. RTU Schematic

The coarse coal contacting vessel T-6 is a heated and insulated tank in which hot reagent may flow through a bed of retained coarse coal. This unit is used principally to convert regenerated leach solution in storage tanks T-7 or T-8 to a more depleted solution simulating recycle reagent after secondary reaction. This capability is required since R-2 is not utilized during all experimentation. T-6 is basically a coarse coal reactor and, if appropriate sampling ports and possibly some flow distribution internals were added, it could be used to obtain design data for coarse coal processing.

Detailed descriptions of the principal RTU coal processing operations are presented in the ensuing sections.

### 4.1.1 Coal Feed System

Process feed coal is transported from the Ultrasystem's coal grinding facility located in Irvine, California, to the Capistrano Test Site in steel bins which maintain a nitrogen atmosphere to prevent coal weathering. Coal bins are hoisted to the top level of the RTU test stand and emptied by a hydraulic bin tilter-vibrator A-1 (Figures 6 and 7). Dust control is maintained by coupling the bin vent to transport ducting with flexible sleeving.

Coal feed is routed according to the coal top-size. During coarse coal utilization (1/4-inch top size or larger), feed coal is diverted from the bin discharge to the T-6 leach tank where it is contacted with reagent to effect leach solution depletion. Fine coal processing feed material is charged to the coal storage tank T-1 (Figure 8). A vibrating discharge unit A-2 at the bottom of T-1 prevents solids bridging or packing and maintains coal flow to the weigh belt A-3. Fine coal feed is metered by A-3 to a moisture lock rotary valve A-4 which feeds the coal reagent mixing vessel T-2 (Figure 9). The weigh belt is instrumented to display coal feed rates and cumulative coal flow on the plant control panel. All dry coal storage and transfer units downstream of the bin discharge are operated under nitrogen pressure to prevent oxidation of the coal feed.

### 4.1.2 Leach Solution Feed System

Leach reagents utilized during RTU operation were generally blended in the secondary reactor R-2 and pumped to reagent storage tanks via P-7. Iron

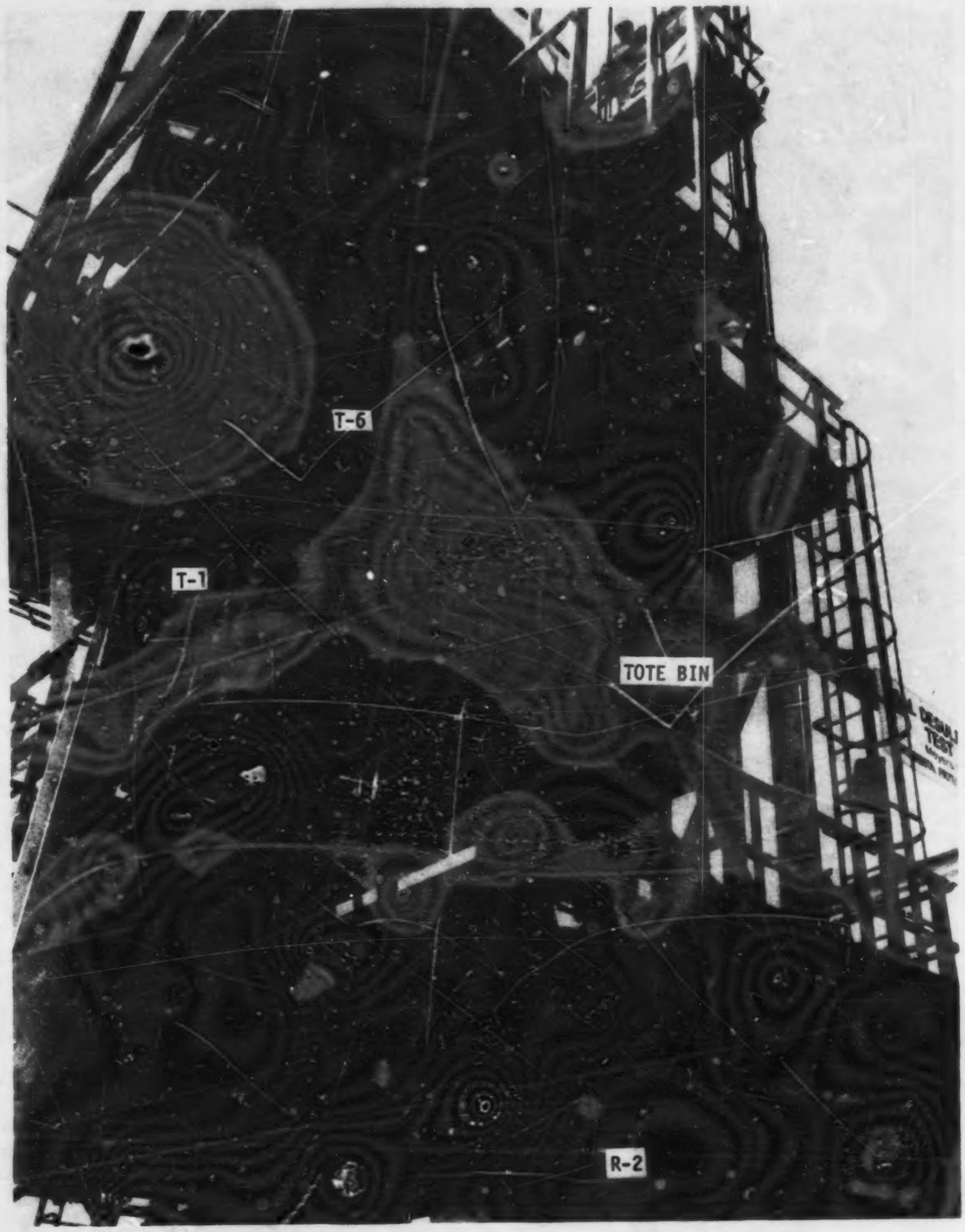

T-6
T-1
TOTE BIN
TEST
R-2

Figure 6. RTU Bin Lift

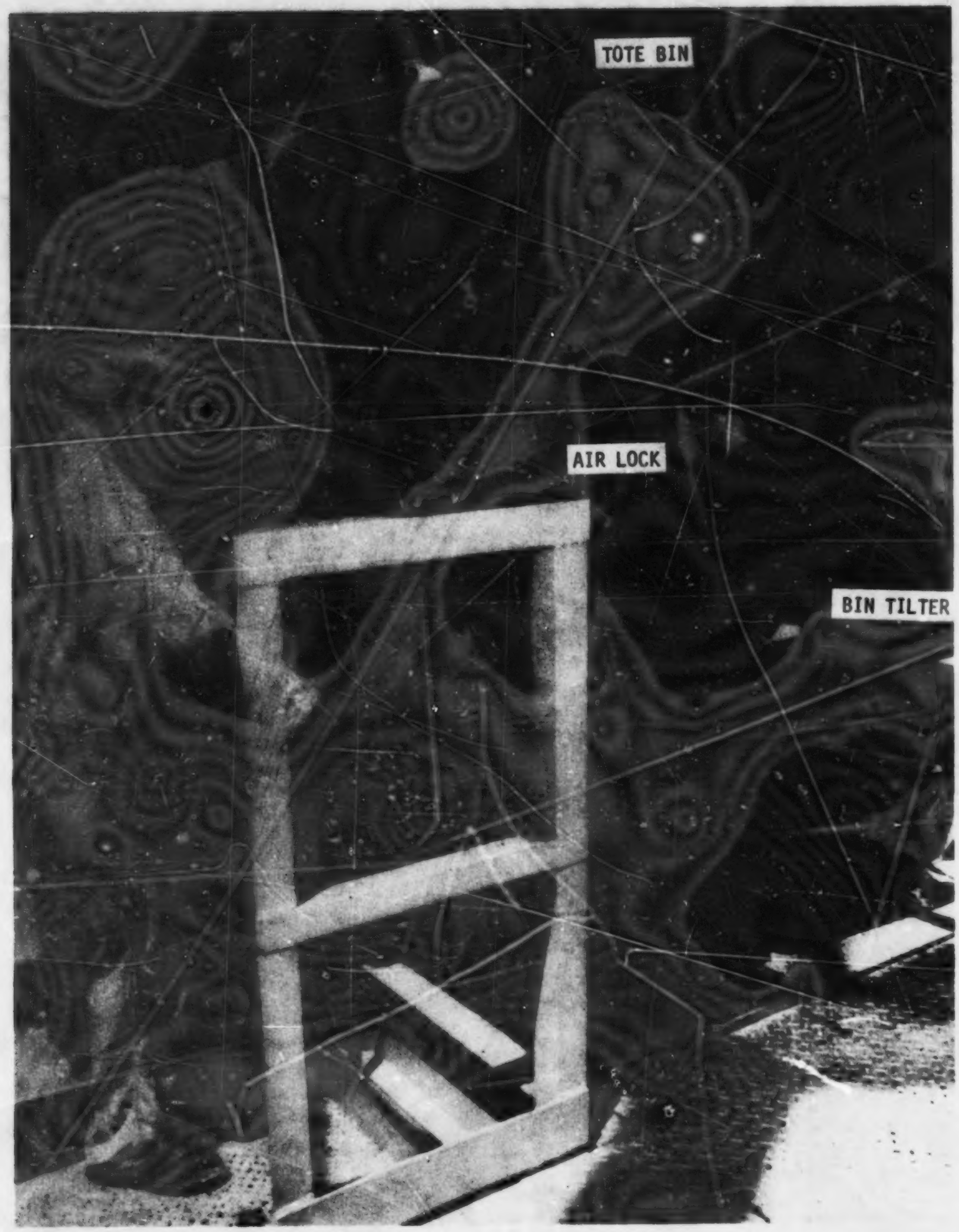

TOTE BIN
AIR LOCK
BIN TILTER

Figure 7. RTU Bin Tilter

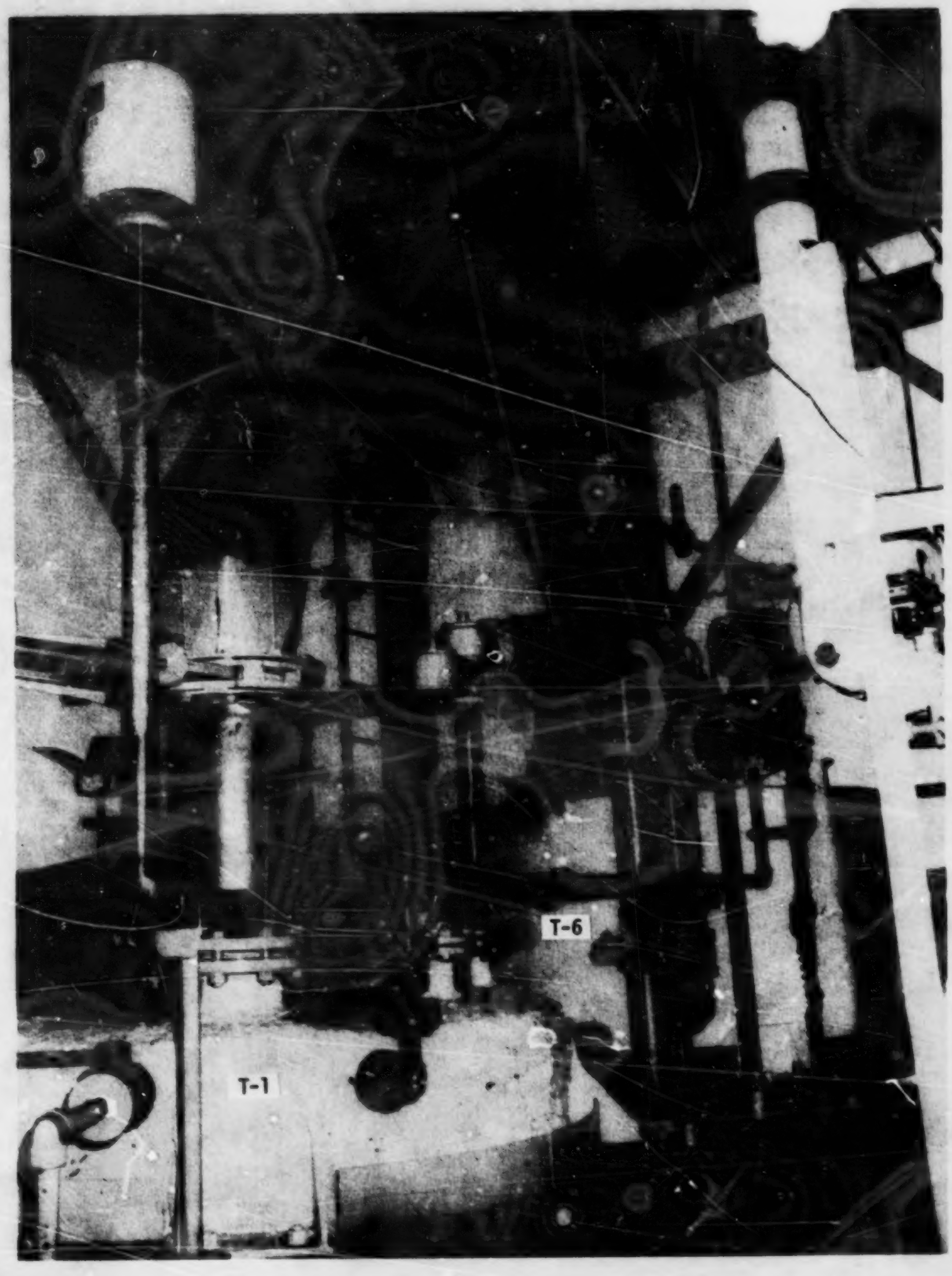


Figure 8. Coal Feed to Fine Coal Storage
and the Coarse Coal Leacher

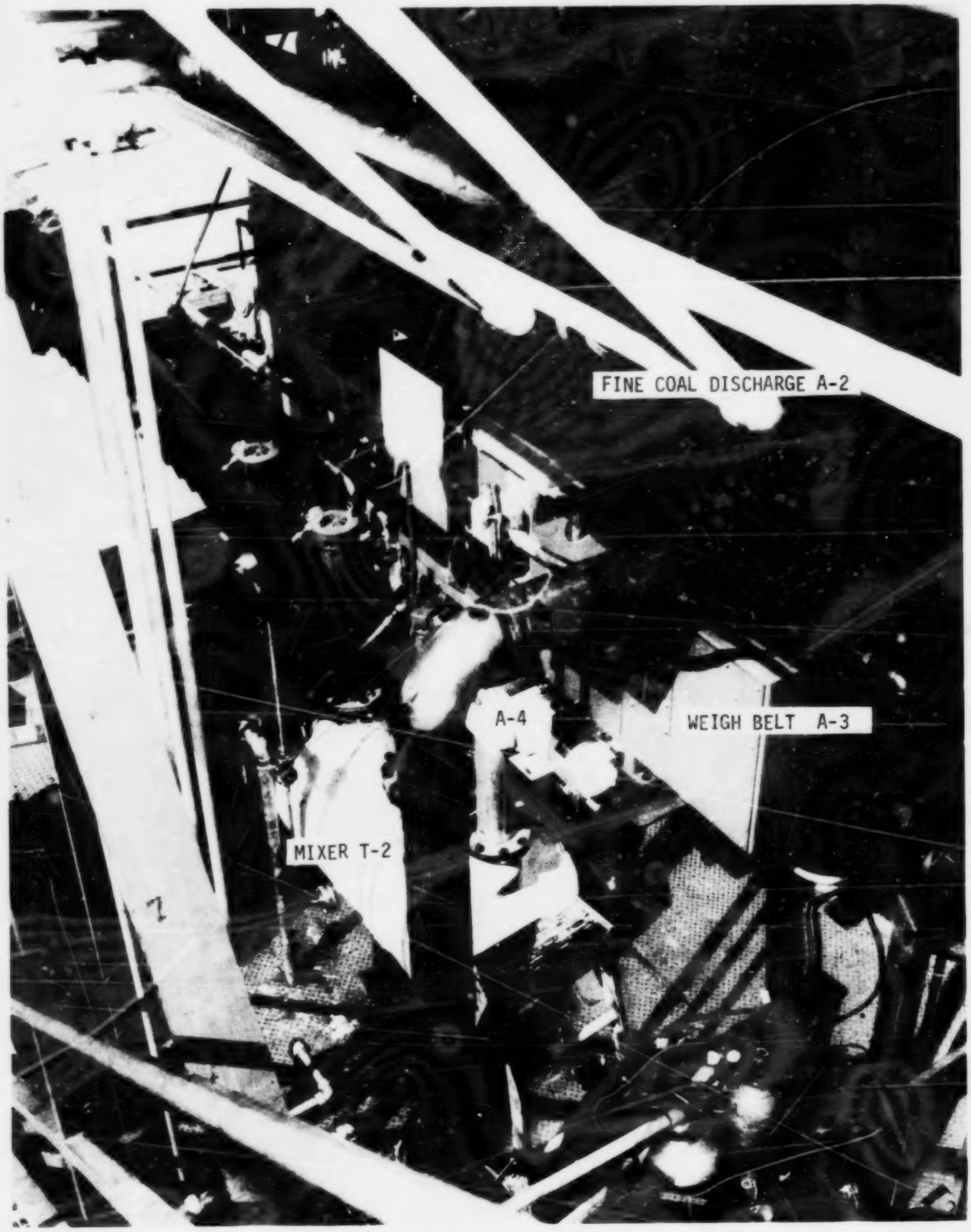

FINE COAL DISCHARGE A-2
A-4
WEIGH BELT A-3
MIXER T-2

Figure 9. Coal Feed To The Mixing Unit

sulfate reagent was stored in leach solution surge tank T-7 while distilled water or iron free leach reagent was stored in surge tank T-8 (Figure 10). Quantities of reagent in storage were monitored with buoyant-type liquid level guages.

Reagent from either T-7 or T-8, as required, was pumped to the reactor system by P-13. Prior to actual coal contacting and reaction, reagent from P-13 was used to break down foam and demist primary reactor vent gases in knock-out drum V-1. Reagent and any entrained mist or foam was brought up to the desired temperature for the first stage of mixing (typically, $170^{o}F$) by heat exchanger E-2 and fed to the foam scrubber T-3 to break down any foam generated during the mixing operation. Reagent was gravity fed from T-3 to the first stage of the T-2 mixer. Reagent feed rates are monitored by a magnetic flow meter located between E-2 and T-3.

### 4.1.3 Oxygen Feed System

Oxygen is stored as a liquid at the RTU facility and vaporized as required for process reagent regeneration. The total flow rate of gaseous $O_2$ (200 psig) to the primary reactor R-1 was monitored by target flow meter FE-61 and feed $O_2$ was subsequently partitioned among the reaction stages with the aid of rotameters FI-62 through FI-66. Oxygen-slurry contacting is achieved by injecting the $O_2$ stream into slurry recirculation loops associated with each reactor stage. The point of $O_2$ injection is located approximately ten feet upstream from the point of slurry reentry into the reactor stage. Slurry recirculation rates were maintained sufficiently high to ensure turbulent flow and vigorous blending of reagent and oxygen.

Unreacted oxygen flows from R-1 through the knock-out drum V-1 and pressure relief valve PV-43 to the vent gas scrubber T-4. Vent gas flow rates from R-1 are measured by target flow meter FE-44 which is located between V-1 and PV-43. The oxygen content of vent gas is measured by the oxygen analyzer AE-171 which analyzes a dried slipstream of the V-1 exhaust.

### 4.1.4 Process Steam

Steam for process heating was generated by a Clayton steam generator which had the capability of generating 1000 pounds of 150 psig steam per

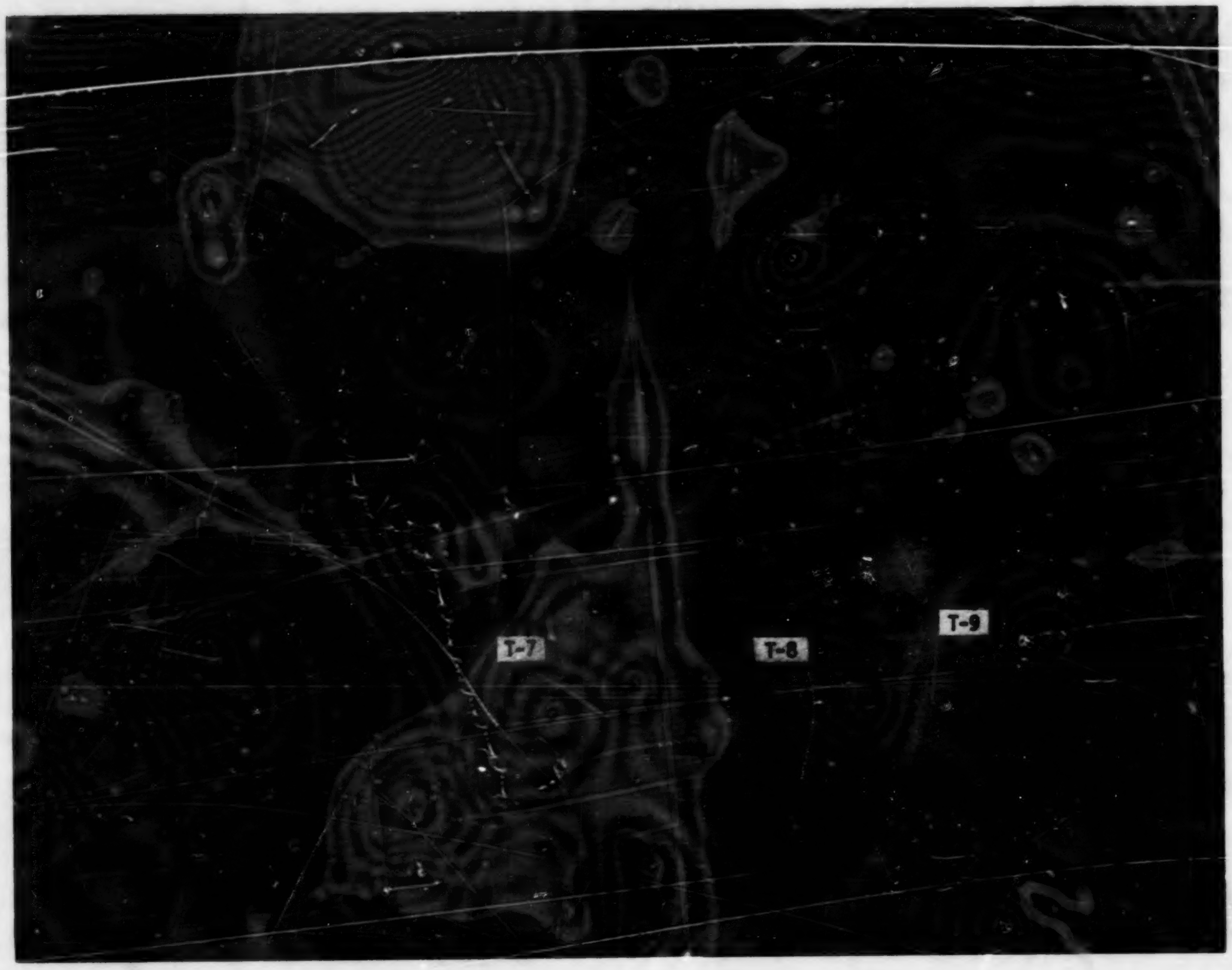


Figure 10. RTU Tank Farm

hour. A majority of the process steam required is used for direct contact heating of slurry streams and wet coal cakes although several heat exchangers are used in the RTU. Flow rates of steam into T-2 and R-1 for direct contact heating are measured with rotameters FI-16 through FI-18 and FI-67 through FI-71, respectively. Steam feed rates are set and maintained manually. Flow rates of steam into heat exchangers are regulated by temperature actuated flow controllers.

### 4.1.5 Coal-Reagent Mixing

Initial coal-reagent contacting, coal wetting and slurry defoaming were performed in the mixing unit T-2 under atmospheric pressure (Figure 11). The mixer is partitioned into three stages by weirs which may be adjusted to vary stage volumes and, consequently, slurry retention times. Each stage is equipped with a variable speed mixer to promote coal wetting and prevent settling. Slurry temperature was increased stagewise from approximately 170°F to the solution normal boiling point (nearly 214°F for iron sulfate reagents) by direct contact heating. Shielded thermocouples are situated in each stage of T-2 to permit continuous monitoring of slurry temperature. Gases or foam generated in T-2 are treated by the foam scrubber T-3 and subsequently by the vent gas scrubber T-4.

Thoroughly wetted slurry was pumped from T-2 to the primary reactor R-1 by slurry pump P-1. The rate at which slurry was pumped through P-1 was regulated by slurry level controller LIC-26 in the third stage of T-2.

### 4.1.6 Primary Reaction and Reagent Regeneration

Simultaneous coal leaching and reagent regeneration were performed in the primary reactor at nominal temperatures up to 270°F and pressures up to 100 psig. Design capabilities of R-1 are somewhat higher with a maximum temperature and pressure of 300°F and 150 psig, respectively. The R-1 reactor consists of five stages separated by weirs. All five stages may be used for reaction or, alternately, the P-1 slurry feed may be diverted around the first two stages of R-1 to effectively yield a three-stage reactor. Each reaction stage is a continuous flow stirred tank reactor in which agitation is achieved by means of a variable speed mixer and a slurry recirculator. The slurry recirculation loops are also used for steam

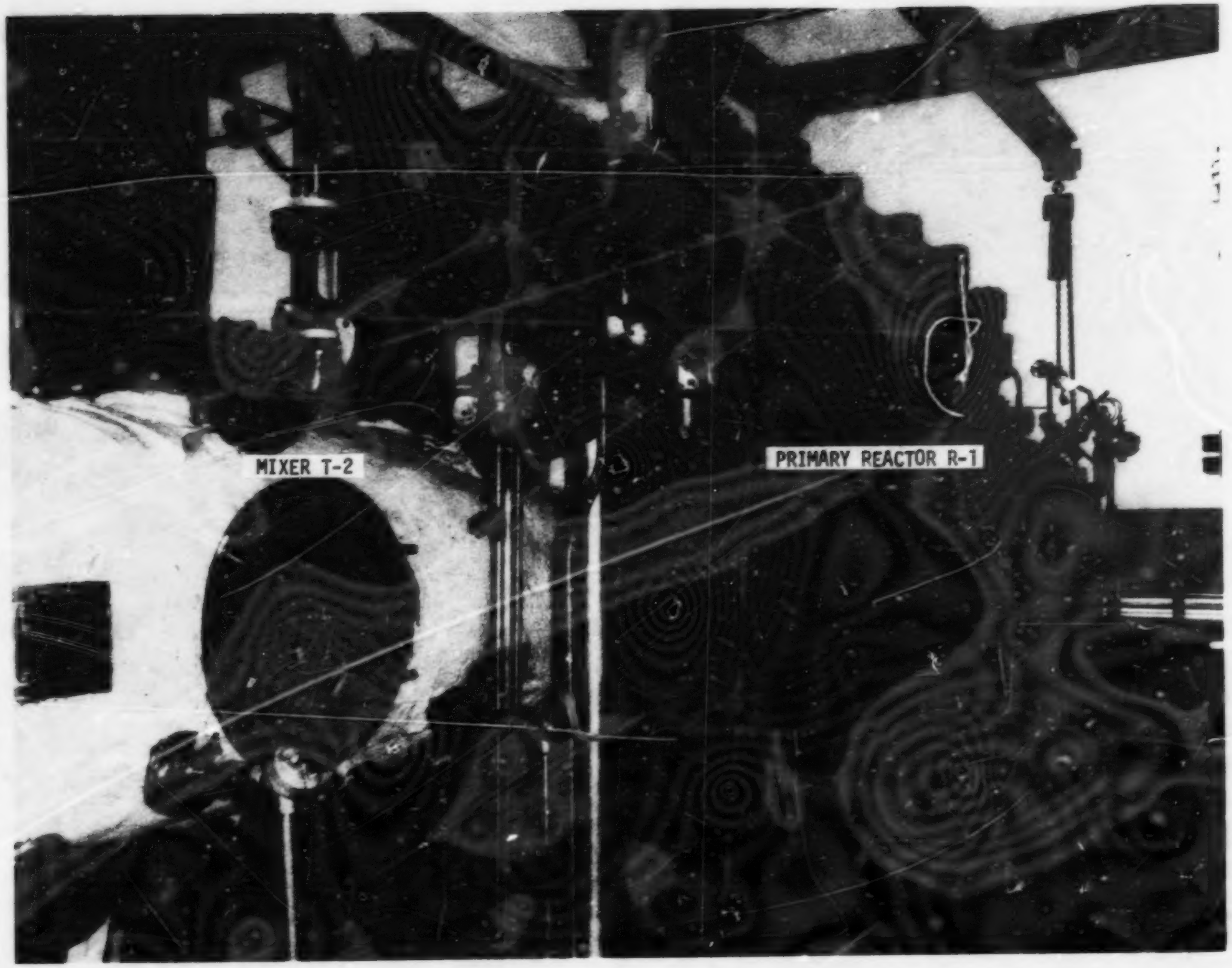

MIXER T-2
PRIMARY REACTOR R-1

Figure 11. RTU Mixer and Primary Reactor

injection to maintain reaction temperature and oxygen injection for reagent regeneration.

Reaction stages of R-1 have interconnected overhead ullage and, therefore, all stages are operated at the same pressure. R-1 vents to the knock-out drum V-1 which demists vent gases and breaks down any foam which may be generated during processing. Vent gases leaving V-1 are further processed in the vent gas scrubber T-4.

Processed slurry is flashed from the fifth stage of R-1 into the slurry flash drum T-5 which is maintained at atmospheric pressure. Vent gas and flashed steam from T-5 are processed through T-4. Underflow slurry from T-5 is gravity fed to either the secondary reactor for further processing or the filtration unit S-1. Slurry is flashed from R-1 in pulses having durations of up to three seconds with approximately 25 seconds between pulses.

### 4.1.7 Secondary Reaction

Coals requiring further processing after primary reaction in R-1 are gravity fed from the flash drum T-5 to the secondary reactor R-2 for batch processing. Reaction in R-2 may be carried out at temperatures up to 250°F in the absence of oxygen. Alternately, at temperatures below 250°F, oxygen partial pressures may be maintained such that the system total pressure does not exceed 14 psig. Reaction temperatures in R-2 are maintained by electrical heating tapes at the reactor surface to enable prolonged processing without the slurry dilution inherent to direct steam heating. Slurry agitation is provided by a single variable speed mixer. R-2 vent gases are processed through the vent gas scrubber T-4. Fully processed slurry may be pumped from R-2 to either the filtration unit S-1 or to waste disposal T-9. When not in service as a reaction unit, R-2 may be utilized for reagent formulation and mixing.

### 4.1.8 Filtration and Leach Solution Recovery

Processed slurries from the primary reactor R-1 (via flash drum T-5) or from the secondary reactor R-2 were fed to the filtration unit S-1 for reagent recovery and coal washing (Figure 12). S-1 is a belt-type filter with two filtration zones having discrete filtrate collection systems. The first filtration zone is for recovery of concentrated reagent which is

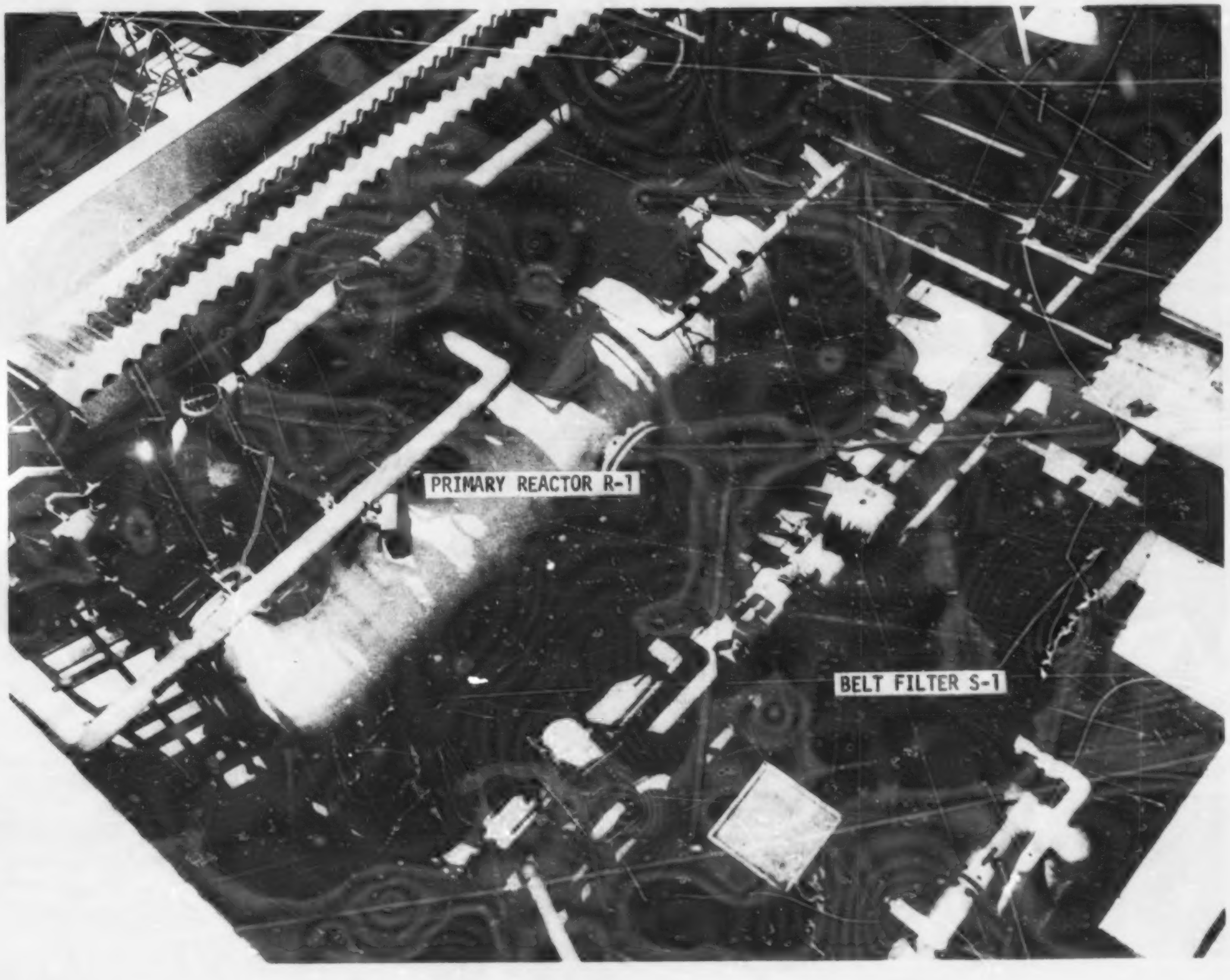

PRIMARY REACTOR R-1
BELT FILTER S-1

Figure 12. Primary Reactor and Belt Filter

collected in a filtrate receiver V-2 (Figure 13) and recycled back to the appropriate leach solution surge tank T-7 or T-8. The second filtration zone is for recovery of hot wash water which is sprayed on the coal filter cake to effect further reagent recovery. Filtrate from coal cake washing is collected in the wash water receiver V-3 and pumped to disposal tank T-9. Vacuum for filtration was provided by vacuum pump K-1 which couples to the filtrate receivers V-2 and V-3. Steam is applied to the coal cake during filtration and washing to prevent cracking of the filter cake and maintain cake temperatures of approximately 180°F.

The spray-washed coal cake was scraped from the filter belt and loaded into storage containers or disposal dumpsters. Residual solids adhering to the filter belt were removed with water sprays directed at the inner and outer belt surfaces. The low solids slurry resulting from belt washing may be recycled for cake wash to minimize losses of process solids or disposed of directly.

Those process products not required for process characterization or vendor testing were disposed of at class "A" landfills. Low solids content liquid wastes from T-9 were disposed of by Industrial Trucking Co., Wilmington, California. Discard coal cake was disposed of by Removal Inc., Lawndale, California.

### 4.1.9 Coarse Coal Leaching and Reagent Depletion

Depleted leach solution for recycle reagent simulation is generated in the coarse coal leach tank T-6. Coarse coal is loaded into T-6 from the bin tilter A-1 and may be preheated with steam which is introduced at the reactor bottom. Hot leach solution from heat exchanger E-2 contacts the coarse coal bed at the bottom of T-6, flows upward through the bed and is pumped to reagent storage in T-7 or T-8. Alternately, reagent may be retained in T-6 for batch leaching. Spent reagent may be drained from T-6 through a screened drain port at the vessel bottom. Near complete recovery of spent reagent is effected by washing with water which flows upward through the coal bed. Processed coal is discharged from the bottom of T-6 into a dumpster for sampling and/or disposal.

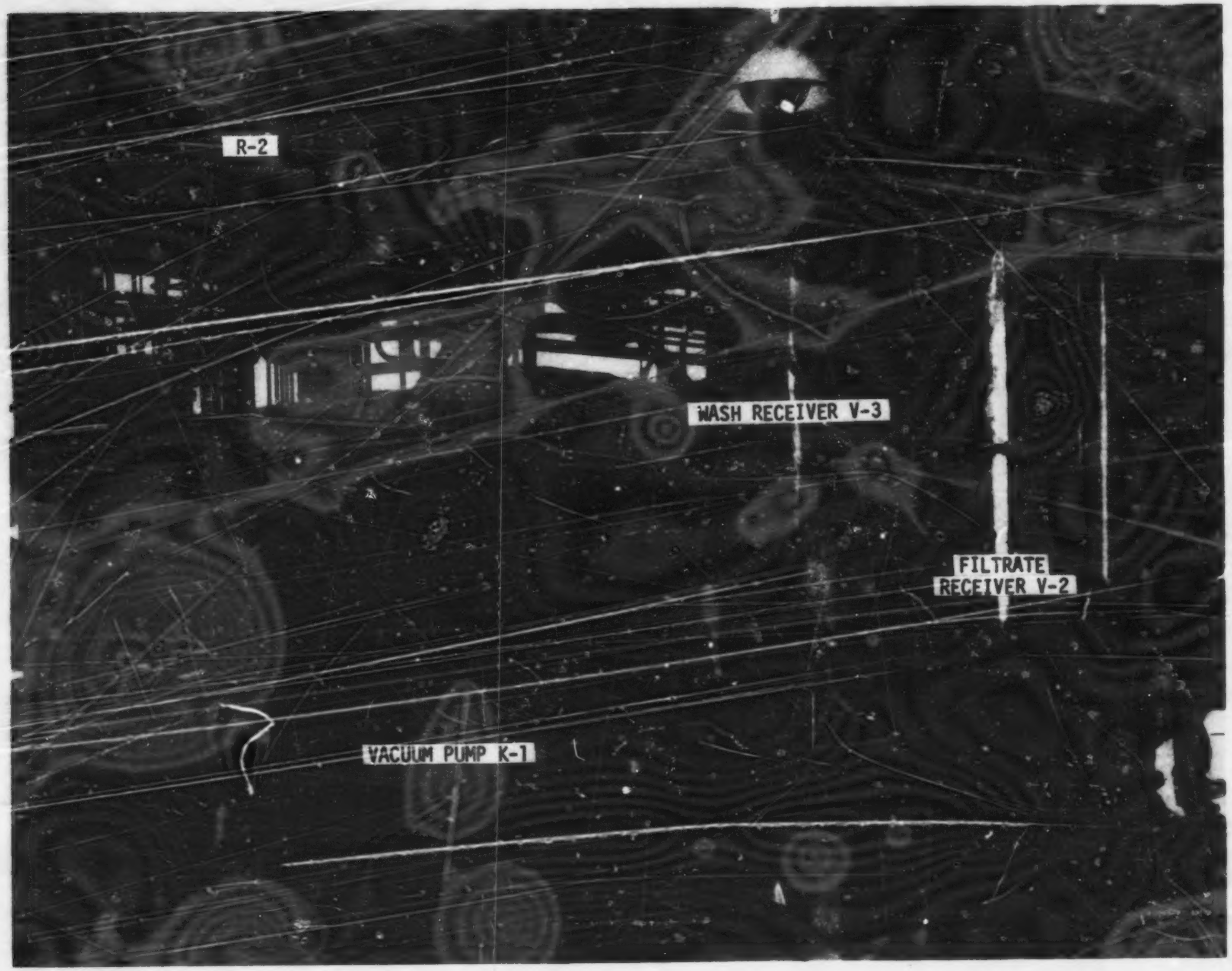

R-2
WASH RECEIVER V-3
FILTRATE RECEIVER V-2
VACUUM PUMP K-1

Figure 13. Vacuum Pump and Filtrate Receivers

### 4.1.10 Instrumentation

RTU instrumentation may be classified according to relative importance of instrument function during plant operation. Primary instrumentation requires continuous monitoring for maintenance of plant operational safety and/or acquisition of data required for process evaluation. Data from primary instrumentation are displayed at the plant control panel either in digital, gauge or printed tape form, and are also recorded on magnetic tapes for subsequent evaluation (Figure 14). Additionally, primary data are generally displayed on the test stand to facilitate plant operation and local monitoring. Examples of primary data sources include the weigh belt coal feed rates, magnetic flow meters measuring reagent and slurry feed rates, thermocouples monitoring reaction temperature, transducers monitoring reactor pressures and level gauges indicating slurry depths in the mixer and reactors.

Secondary data sources are those providing information which is not critical to safe plant operation or process evaluation. These data sources are not monitored continuously with some being checked on a daily or weekly basis. Data acquisition from secondary sources usually consists of manual recording and tabulation. Examples of secondary data sources include flow meters indicating seal flush water flow rates, steam flow meters and reagent storage tank level indicators.

### 4.1.11 Process Sampling and Analysis

All major RTU processed solid, liquid, slurry and gas streams were sampled and analyzed during plant operation. Analyses of solid and liquid streams were performed at the RTU control laboratory. Additionally, selected coal samples were analyzed by Warner Laboratories, Cresson, Pennsylvania. Gas sampling and analysis was performed on a continuous basis by RTU equipment.

Sampling ports available for acquisition of feed reagent samples are located at the leach solution feed pump P-13 and at the foam scrubber T-3. Feed solids are sampled with a full stream coal diverter located at a point between the weigh belt A-3 and rotary valve A-4. Stream diversions of up to one minute were used during normal sampling although longer periods of time were used during A-3 calibration. Slurry samples were drawn from the mixer T-2 through sampling ports located in the wall of each mixing stage. Primary

Figure 14. RTU Control/Instrumentation Console

reactor R-1 slurry samples may be drawn from each stage through wall sampling ports or by full stream diversion of slurry passing through recirculation loops. Processed slurry sampling ports are located in the slurry flash drum T-5 and in the secondary reactor R-2. Processed coal samples may be taken directly from the filter belt S-1 after the spray wash operation.

Feed coal samples were submitted for short proximate analysis (moisture, ash, heat content and total sulfur analyses), sulfur forms analysis (pyritic and sulfate sulfur analysis), ash iron content analyses and size distribution determination. Reagent samples, whether feed reagent or slurry sample filtrates, were analyzed for total iron, iron forms, sulfate content and pH. Slurry samples were analyzed for solids content and slurry solids were water washed, extracted with toluene and dried. Dry slurry solids received short proximate, sulfur forms and ash iron analyses. Residues from toluene extracts were analyzed for total sulfur content.

Vent gas from R-1 was continuously sampled by means of a slipstream taken immediately downstream from V-1. The sample slipstream was dried and subsequently analyzed for oxygen content by a Taylor oxygen analyzer. Gas analysis results were continuously displayed at the plant control panel.

## 4.2 PROCESS EQUIPMENT

Detailed mechanical design specifications, drawings, and vendor prints for all RTU equipment have previously been submitted to the EPA (TRW-Procon Design Drawings, Vendor Prints, and Design Specifications). These documents contain plant plot plans, mechanical flow diagrams, civil and structural drawings, mechanical, electrical and instrument drawings, piping diagrams and vendor data. Detailed specifications for all equipment, piping, electrical, and instrumentation installations are also included. Descriptions of services provided on a regular basis in support of RTU operation as well as stepwise procedures have been documented. This extensive documentation is not replicated in this report but is mentioned for reference only. However, specifications of principal coal processing equipment utilized during RTU operation are summarized in this section to provide definition of the RTU processing capabilities. The ensuing sections will also describe the various support facilities utilized during RTU operation.

### 4.2.1 Coal Transport Bins

Seventy-five coal transport bins were fabricated of carbon steel. Bin dimensions are 42" x 48" x 96" (H) which provide approximately 112 cubic feet of storage space. Coal bins are designed to receive coal ranging from 3/8-inch top-size to 100 mesh top-size. Each bin is equipped with a 12-inch diameter opening located at the top for coal loading and a 34-1/4-inch x 14-11/16-inch (H) trap door on the side of the bin near the bottom for coal discharge. Coal bins are airtight and equipped with gas inlet and outlet fittings to enable slight pressurization with nitrogen.

### 4.2.2 Bin Tilter

The bin tilter A-1 is a steel frame capable of handling a fully loaded bin and equipped with a pneumatically operated tilting mechanism. A-1 is equipped with leg clamps which automatically seal the bin to the feed hopper gasket and prevent dust emission to the atmosphere during the coal discharge operation. The A-1 vibrator maintains coal solids flow once the bin discharge door is opened.

### 4.2.3 Coal Storage Tank

Coal is stored in a vertical carbon steel tank T-1 which is a 6-foot diameter cylindrical vessel with a conical bottom to facilitate coal discharge. T-1 has a total volume of approximately 180 cubic feet. The T-1 vessel receives coal from the coal feed chute through a 1-foot square opening in its top. T-1 is equipped with a live bin bottom capable of maintaining variable solids discharge flow rates without bridging or packing. The T-1 discharge unit A-1 is equipped with a two-point cycle timer to regulate the discharge oscillator. A-1 is capable of maintaining coal discharge rates from 250 to 1000 pounds per hour. T-1 is maintained under a slight nitrogen pressure (up to 6 inches water column) to prevent coal oxidation. Maintenance of an adequate quantity of coal in T-1 is ensured by monitoring the coal level with a sonic level switch which activates a low level alarm.

### 4.2.4 Weigh Belt

An Autoweigh weigh belt A-3, capable of metering coal flow rates up to 1000 pounds per hour, transfers coal fed from the coal storage tank T-1 to the rotary feed valve A-4. A-3 is designed to transfer ground coal from

8 mesh to 100 mesh in top-size. A belt speed monitor and strain-gauge load cell are used to provide coal feed rate and total coal feed outputs, and to signal a feedback controller which maintains preset coal feed rates by adjusting the belt speed. Coal feed rate monitoring accuracy is within 0.5% of the actual coal feed rate. The A-4 feed valve is airtight and acts as a moisture barrier between A-3 and the first stage of the slurry mixing unit T-2. Both A-3 and A-4 are operated under a nitrogen atmosphere. A full stream butterfly valve coal diverter is located between A-3 and A-4 which enables acquisition of feed coal samples.

### 4.2.5 Tank Farm

Leach solution and process liquid wastes are stored in a tank farm consisting of three glass-fiber reinforced polyester tanks T-7 through T-9. Each tank is 12 feet in diameter, 20 feet high and has a storage capacity of 16,000 gallons. These tanks are designed for atmospheric pressure service at up to 200$^0$F. Stored solution volumes are measured by Varec liquid level gauges and are accurate to approximately 5 gallons. Tank farm plumbing is designed to enable solution transfer among the storage tanks.

### 4.2.6 Leach Solution/Slurry Pumps

Sixteen process pumps are included in the RTU for either liquid (water or reagent) or slurry service. These pumps are largely centrifugal and progressive cavity-type pumps although diaphragm and regenerative pumps are also used. Pumps used in acid reagent service were constructed of 316L S.S. while those in water service were fabricated of cast iron or other less noble materials. Specific data for each pump are listed in Table 1.

Centrifugal pumps were utilized for low head pressure and moderate or high flow rate applications such as R-1 slurry recirculation and liquid waste disposal. Nine centrifugal pumps were utilized in the RTU with eight being used for slurry/reagent pumping service (P-2 through P-6, P-9, P-12 and P-14) and one being used in very dilute reagent service (P-10). Progressive cavity pumps were utilized for pumping slurries at low flow rates against large head pressures as encountered in feeding slurry to the pressurized primary reactor through P-1. To provide possible replacement units for P-1, two progressive cavity pumps were also used in less severe applications (P-7 and P-13). Two

## TABLE 1. RTU PUMP DATA

| Pump Identification | Description | Manufacturer | Type | Design | | Driver, H.P. | Material of Construction |
|---|---|---|---|---|---|---|---|
| | | | | Capacity, gpm | $\Delta P$, psi | | |
| P-1 | Slurry feed pump | Moyno | Progressive cavity | 1.1-4.6 | 140 | 3 | 316 SS |
| P-2 through P-6 | Slurry recirculation | Dean Brothers | Centrifugal | 25 | 33 | 2 | 316 SS |
| P-7 | R-2 discharge pump | Moyno | Progressive cavity | 1.1-4.6 | 140 | 3 | 316 SS |
| P-8 | Filter wash pump | Warren Rupp | Diaphragm | 10 | 40 | Air drive | 316 SS |
| P-9 and P-10 | S-1 filtrate pumps | Duriron | Centrifugal | 20 | 40 | 5 | Durcomet 100 |
| P-11 | Reagent recirculation pump | Warren Rupp | Diaphragm | 5 | 18 | Air drive | 316 SS |
| P-12 | Reagent circulation pump | Dean Brothers | Centrifugal | 20 | 18 | 2 | 316 SS |
| P-13 | Reagent feed pump | Moyno | Progressive cavity | 0-8.4 | 140 | 1.5 | 316 SS |
| P-14 | Waste disposal pump | Dean Brothers | Centrifugal | 200 | 32 | 7.5 | 316 SS |
| P-15 | Cooling water pump | Paco | Turbine | 100 | 250 | 15 | Cast iron |
| P-16 | Seal flush water pump | Aurora | Regenerative turbine | 12 | 150 | 5 | C.I./Bronze |

diaphragm pumps were utilized in the RTU for low head pressure, low flow rate applications (P-8 and P-11). One regenerative turbine pump (P-16) was utilized for a seal flush water pump due to its high head pressure, low flow rate characteristics and one turbine pump (P-15) was used for cooling water circulation.

### 4.2.7 Heat Exchangers

Two process streams are heated by jacketed pipe heat exchangers: 1) feed reagent to T-3 is heated in E-2 and 2) filter belt wash water is heated in E-3. The heating fluid for both exchangers is 150 pound steam and each is designed for a maximum temperature and pressure of 400°F and 200 psi, respectively. Exchanger E-2 consists of two heat exchangers in series, each of which is 30 inches long having a 3/4-inch Sch. 40 pipe of 316 S.S. and a 1.5-inch Sch. 80 jacket of carbon steel. Exchanger E-3 consists of three heat exchangers in series, each of which is 45 inches long having a 3/4-inch Sch. 80 pipe and a 1.5-inch Sch. 80 jacket. E-3 is all carbon steel construction since it is not subjected to a corrosive environment.

The primary reactor R-1 is equipped with jacketed pipe heat exchanger E-1 to provide for removal of excess heat of reaction. E-1 consists of four heat exchangers in series which may be divided among the R-1 slurry recirculation loops. Each segment of E-1 is 3.5 feet in length having 1.25-inch Sch. 40 pipe of 316 S.S. and 2-inch standard weight carbon steel jacketing. E-1 is cooled with site cooling water and is designed for pipe temperatures and pressures up to 300°F and 150 psi.

A shell and tube heat exchanger E-4 is used to cool flush water for pump and mixer seals. This unit is cooled with site cooling water. Shell material is bronze and tubing is admiralty brass. E-4 is designed for temperatures and pressures of up to 300°F and 150 psi.

### 4.2.8 Slurry Mixing Tank

Coal-reagent mixing and preheating takes place in the mixing tank T-2. The mixer is a three-stage, 316L S.S. horizontal vessel having a diameter of 2.5 feet and length of 7.5 feet. The stages are separated by adjustable weirs with which the stage volumes and, therefore, slurry residence times may be varied. Weir heights may be adjusted from approximately 10 to 23 inches. Each stage of T-2 is equipped with a variable speed 3/4 horsepower Lightnin agitator capable of up to 350 rpm. Live steam for slurry heating is injected into each stage of T-2 through nozzles in the vessel wall. All stages of T-2 vent through a common foam scrubber T-3 and through a vent gas scrubber T-4.

Each stage of the mixer is equipped with a slurry sampling port, drain port and a thermocouple probe. The third stage of T-2 contains an Air Products bubble tube-type level indicator and an auxiliary stilling well.

### 4.2.9 Reactors

Three reactors are utilized in the RTU: (1) the primary fine coal reactor R-1; (2) the secondary fine coal reactor R-2; and (3) the coarse coal leacher T-6. RTU reactors are constructed of 316L S.S. and are rated for processing temperatures of up to 300°F. All RTU reactors are insulated with 1.5 inches of urethane foam.

The primary fine coal reactor is a horizontal pressure vessel with a diameter of 38 inches and a length of 14.75 feet. R-1 is designed for pressures up to 150 psig and for full vacuum (to accommodate hot lockup and subsequent depressurization through cooling). Composed of five stages, R-1 is partitioned by stationary weirs which are 28.5 inches in height. Slurry feed lines are plumbed to allow bypass of the first two R-1 stages and provide for three stage processing. Each stage of R-1 is agitated by a variable speed 1.5 horsepower Lightnin mixer and a slurry recirculation system. Four baffles are spaced around each stage to promote efficient slurry mixing. Slurry level in the fifth stage is measured by an Ashcroft buoyant type level gauge. R-1 slurry is discharged from the fifth stage to flash drum T-5 either by flashing through a 1-inch ball valve KV-241 or by pumping slurry through the fifth-stage recirculation pump P-6.

Reactor heating and slurry oxygenation are performed by injecting steam and oxygen into the slurry recirculation loop of each R-1 reaction stage. Reactor temperatures are monitored by thermocouple probes installed in each R-1 stage. R-1 stages vent to a common foam knock-out drum V-1 and vent gas scrubber T-4. Reactor pressure is maintained by a Masoneilan control valve and is monitored by a transducer PT-173 located at the reactor vent.

R-1 is equipped with 1-inch sampling ports in the vessel wall and in the slurry recirculation loops. Recirculation loop sampling ports enable full stream bypass through a sampling unit which is ultimately isolated and drained.

The secondary fine coal reactor is a vertically oriented cylindrical vessel with a conical bottom. R-2 has a diameter of 3.5 feet and has a height of 4.1 feet (T/T); the corresponding volume of R-2 is 365 gallons. R-2 is designed to maintain 14 psig or full vacuum. Reactor pressures are monitored by an Ashcroft pressure gauge PI-98. R-2 agitation is provided by a variable speed 1-1/2 horsepower Lightnin mixer. Three baffles are distributed within R-2 to prevent channeled flow and promote efficient mixing.

Slurry enters R-2 through a 2-inch nozzle at the reactor top and discharges through a 1.5-inch nozzle at the reactor bottom. Slurry levels in R-2 are monitored with an Air Products bubble tube level sensor LT-95. Slurry temperatures are monitored with a thermocouple probe TE-99.

The coarse coal leach solution depleter T-6 is a vertically oriented cylindrical vessel with a conical bottom. The vessel diameter is 5 feet and the straight side height is 5 feet. T-6 is essentially an atmospheric pressure vessel. Coal enters T-6 through a 12-inch square chute at the vessel top and is discharged through a 12-inch knife valve at the bottom. Reagent enters and discharges from T-6 through 3/4-inch ports at the bottom and top of the vessel, respectively. T-6 is heated by live steam injected through a 1-inch port at the vessel bottom. Reaction temperatures are monitored with a thermocouple probe in the vessel wall. Reagent may be drained from T-6 through a 3/4-inch drain port equipped with a 2-inch duplex strainer for retaining coal. Reactor pressure is monitored with an Ashcroft mechanical pressure gauge PI-260.

### 4.2.10 Flash Drum

The slurry flash drum T-5 is a vertical vessel with a conical bottom. T-5 has a 3-foot diameter and a height of 3.7 feet (T/T). T-5 is designed for up to 14 psig pressure and full vacuum. Flash slurry enters T-5 through a 2-inch nozzle located 1.7 feet below the upper straight side end. A porous demister pad is situated immediately above the flash slurry inlet to minimize slurry entrainment. Slurry level is monitored in T-5 and an alarm condition results if slurry levels rise appreciably above the conical vessel bottom.

### 4.2.11 Scrubbers

Slurry foam control and acid mist elimination are obtained in the RTU with three scrubbers: (1) the foam scrubber T-3; (2) the knock-out drum V-1 and (3) the vent gas scrubber T-4. T-3 is a 316L S.S. vessel of 1-foot diameter and 4 feet in height. A single bubble cap tray is used to break down foam generated in the mixer T-2. Designed for gas flow rates of 30 SCFM and liquid flow rates of 2.5 gpm, T-3 may be operated under full vacuum or at pressures up to 14 psig with temperatures up to 300°F. V-1 is a 316L S.S. vessel having a 1-foot diameter and a height of 6.5 feet. Two bubble cap trays are used to break down foam and remove acid mist from the R-1 effluent gas. V-1 has the same design pressure and temperature requirements as R-1, namely, full vacuum to 150 psig at temperatures up to 300°F. T-4 is a low pressure FRP vessel having a diameter of 1.5 feet and a height of 4.5 feet. Vent gases flow upward through a 3.5 cubic foot volume of 316 S.S. flex ring packing which is sprayed with cooling water from an overhead nozzle. Operating temperatures in T-4 may range up to 215°F.

### 4.2.12 Filter and Vacuum System

Solid-liquid separation is performed with a belt filter supplied by Ametec. The filter belt consists of a polypropylene mesh cloth 1 foot in width which is supported and conveyed by a channeled plastic belt. The filter is driven by a two horsepower variable speed belt drive. Filter belt speeds may be varied from 1 to 10 feet per minute producing coal cake thicknesses of up to 3 inches. Suction is applied to the belt by means of two vacuum pans over which the belt must pass sequentially. The first vacuum pan is for collection of concentrated reagent while the second collects wash water from the filter cake rinse. Feed slurry is distributed on the belt by a stationary spreader. After initial dewatering, the filter cake is steamed and sprayed with hot wash water by overhead nozzles. The filtration unit is completely enclosed in a reinforced fiberglass hood to prevent steam losses. Sampling ports are built into the hood to permit processed coal sampling before and after the washing operation. Filter belt washing nozzles are located at the belt return immediately beyond the processed coal discharge chute to remove remaining coal particles from the belt and prevent blinding.

Vacuum is supplied to the filter vacuum pans through the respective filtrate receiving vessel (V-2) and wash water receiving vessel (V-3). The filtrate receiver is a 316L S.S. vessel with a 1.2-foot diameter and a height of 5 feet. The wash water receiver is a 316L S.S. vessel with a diameter of 2 feet and a height of 6 feet. Both receiving vessels are under vacuum provided by a

50 horsepower 630 ACFM Nash pump K-1 which is capable of maintaining vacuum of 22 inches Hg. Each receiving vessel is equipped with a demister pad to prevent liquid entrainment into K-1. The contents of V-2 are recycled to reagent storage tanks T-7 or T-8 while the V-3 underflow is pumped to waste disposal.

### 4.2.13 $O_2/N_2$/Air Supply Systems

Gaseous oxygen is supplied to the primary reactor R-1 from a liquid oxygen (LOX) storage tank which is remote from the RTU coal processing facility. The LOX is vaporized and supplied to the RTU at 200 psig. Oxygen feed rates are monitored by a Ramapo target flow meter to ±0.5 percent. Process nitrogen is stored in liquefied form and vaporized for plant use. Nitrogen flow monitoring equipment is identical to that used for oxygen monitoring. Nitrogen is supplied to the plant at 200 psig. Air is supplied to the facility at 125 psig by a 100 SCFM Rand air compressor and is used primarily for equipment drive and valve actuation purposes.

### 4.2.14 Steam Supply System

Process steam is supplied by a Clayton steam generator with the capability of generating 1000 pounds of 150 psig steam per hour. The steam generator is equipped with self-contained water softener and boiler treatment subsystems. The generator is powered by a propane burner also supplied by Clayton Manufacturing Co. Steam feed rates to the RTU are monitored by Brooks rotameters.

### 4.2.15 Process Water System

Two water sources were utilized during RTU operation. The first, an existing well water supply, is used to supply the steam generator and to maintain the 100-gallon seal flush water supply tank. The second source of process water is the RTU catch basin which is a large hypalon lined reservoir having a width of 30 feet, a length of 80 feet and a depth of 5 feet. Water from the catch basin is used for cooling water in heat exchangers, as scrubber water in T-4 and for filter belt wash water.

### 4.2.16 Instrumentation

Detailed instrumentation listings and specifications are presented in the "TRW-Procon Design Specification" manual. This document contains instrumentation tag numbers, manufacturers, materials of construction, operating ranges and, in many cases, unit schematics. Locations of the various instruments in the RTU are fully detailed in the "TRW-Procon Design Drawings and Vendor Prints" manual, drawing numbers X418455 through X418461. Both TRW-Procon documents have been previously transmitted to EPA.

Principal types of instrumentation located on the RTU include pressure gauges, temperature indicators, level gauges, and flow meters. Ashcroft bellows type pressure gauges were used to monitor nitrogen pressures to coal bin storage and instrument purge streams (i.e., PI-184 and 167). Ashcroft bourdon gauges were utilized in monitoring pump slurry and liquid discharge pressures (i.e., PI-73 through PI-77). Remote monitoring of feed gas pressures and reactor pressures was performed with Viatran transducers. Transducers were also used in conjunction with digital display equipment to provide local data readout.

Three principal types of temperature measurement equipment were utilized during RTU operation: (1) thermocouples, (2) dial thermometers and (3) bulb thermometers. Shielded type K (chromel-alumel) thermocouples provided by Heat Technology were used to monitor mixer and reactor slurry temperatures (TE-19, 20, 21 and TE-52 through 56). Bi-metal dial thermometers by Weston/Disco were used for local display purposes such as monitoring wash water temperatures and reagent storage temperatures. Taylor bulb thermometers in thermowells were utilized in conjunction with temperature controllers such as that controlling steam feed rates to heat exchanger E-2 (TIC-32).

A variety of level gauges were employed to monitor liquid, slurry and coal depths in the RTU tanks and reactors. Foam levels in the mixer could be determined by Jacoby-Tarbox sight glasses installed in the T-2 vent lines. A Masoneilan buoyant level gauge was utilized to monitor slurry levels in the fifth stage of the pressurized primary reactor while differential (bubble tube) level indicators were used in the mixer and secondary reactor. Varec float-type indicators were utilized for monitoring reagent and liquid waste levels in tank farm units. Sonic level probes by National Sonics were utilized to activate high and low level alarms in critical process vessels such as the coal feed tank and the primary reactor.

Steam flow rates were monitored with Brooks rotameters. Water flow rates were monitored with both Brooks and Wallace and Tiernan rotameters.

Additionally, Wallace and Tiernan rotameters were used in some gas flow applications. Fischer and Porter magnetic flow meters were used for all slurry flow rate measurements (FE-29, 83-87) as well as for reagent feed rate measurements (FE-31). Oxygen feed and vent rates were monitored with Ramapo target flow meters FE-44 and FE-61.

Outputs of all primary instrumentation and alarm instrumentation were translated into engineering units and recorded by a Doric data processor. The data processor is of modular construction with a solid-state channel scanner, digitizer, microprocessor-based control circuits, channel display and printer. A total of 99 channels for data storage are available and one additional channel serves a self-check function. The system contains a real-time digital clock providing time data printout in days, hours, minutes and seconds. Channel scan rates may be varied from 2 to 20 channels per second. The system is capable of continuous scanning and logging or periodic logging at intervals of 1, 5, 10, 15, 30 and 60 minutes. Alternately, the system may scan continuously but output only those channels which are beyond preset tolerance limits. When scanning at 2 channels per second, an integral digital strip printer may be utilized to provide hard copy printout; all data are recorded on seven-track magnetic tape, regardless of scan speed or frequency.

### 4.2.17 Control Laboratory

Sampling and analyses of all process solid and liquid streams were performed by personnel from the control laboratory at the Capistrano test site. The analytical capabilities of the 760 square foot control laboratory include coal moisture analyses, total sulfur analyses, sulfur forms analyses (pyritic and sulfate sulfur), slurry solids determination, reagent ferrous iron and total iron analyses, reagent sulfate, reagent pH and coal size distribution analyses. Selected coal samples were submitted to Warner Laboratories, Cresson, Pennsylvania, for coal short proximate analyses (moisture, ash, heat content and total sulfur analyses). Toluene extract residues were also submitted to Warner for total sulfur analyses. All analyses are performed in accordance with standard ASTM methods.

To ensure uniform sampling, sample preparation and sample analyses, standard procedures were prepared and documented. The procedural format is essentially the same for sampling and analyses and includes the following elements:

- Procedural scope describing the operation or operations to be defined.
- Procedural conditions specifying personnel and safety requirements and listing all relevant reference documentation.
- Test requirements including equipment requirements and apparatus configuration specifications.
- Detailed analytical and sampling procedures and operational flow diagrams.
- Data recording format.

A tabulation of the standard analytical and sampling procedures is presented in Volume II, Appendix B.

### 4.2.18 Capistrano Test Site Support Facilities

In addition to the control laboratory which was utilized on a continuous basis, the Capistrano test site also provided a variety of services on an as-needed basis in support of the RTU. The CTS weld, machine, and valve shops were all utilized periodically for quick in situ and remote repairs, uncoded fabrications and equipment maintenance. All RTU instrumentation was calibrated upon receipt by TRW metrology which also provided trouble shooting assistance during plant shakedown and operation. CTS procurement, shipping and receiving, and quality assurance assisted RTU operation by locating replacement parts as needed, identifying specialty fabrication shops and procuring all required chemicals. Site power, water and sanitation facilities utilized during RTU operation were maintained by the CTS maintenance department.

# 5. REACTOR TEST UNIT OPERATION

On May 1, 1977, RTU shakedown activities were initiated. The overall shakedown effort was comprised of a system readiness and safety review, operator training, operating procedure verification, laboratory procedure verification, data acquisition system verification, RTU operability evaluation, and Operational Test Plan revision. By late September, 1977, all objectives of the RTU shakedown were met and the RTU was deemed ready to start the planned operational phase of the project.

Operational testing of the RTU was started on October 1, 1977, and was terminated on January 26, 1978. During that 4-month period, the unit processed 49,700 lbs of coal over approximately 250 hours of operation in increments up to 32 hours each. Sufficient data was acquired during operational periods to allow verification of process chemistry (discussed in Section 6), to parametrically evaluate process variables (Section 6), to determine equipment characteristics, and to generate coal quantities sufficient for vendor testing (Section 9).

The remainder of Section 5 presents a summary of achievements and observations relating to RTU shakedown and operation. Sections 5.1 and 5.2 discuss shakedown and operation activities respectively. Additionally, Section 5.2 presents a detailed description of typical RTU start-up, operations, and shutdown sequences. Equipment operating experience is also delineated. Conclusions which were drawn from the first four months of RTU operational experience are presented in Section 5.3.

## 5.1 RTU SHAKEDOWN ACTIVITIES

The primary objectives of the RTU shakedown activities were to verify unit operability, train and familiarize personnel with process operations, facilities, and procedures, and acquire preliminary system data. Necessary modifications to the operational, smapling, analysis and calibration procedures and to the reactor system itself were made during the shakedown period.

### 5.1.1 RTU Safety Review and Training

A thorough pre-start-up safety review of the dual reactor test system was initiated following completion of plant construction. The Safety Review Team (SRT) was comprised of TRW personnel representing the TRW Health and Safety, Structural Design and Fabrication, and Chemical Engineering Departments, Capistrano Test Site management and other upper management representatives from within TRW operations. Most SRT members were individuals not previously intimately involved in the RTU design and operational decisions, thus limiting possible bias. The review was conducted through study of prepared materials (memos, reports, manuals, etc.) and visual site inspections.

The SRT reviewed all start-up, shutdown and operational procedures and evaluated the unit operations from chemical (corrosion, flammability, acidity, etc.) and toxicological standpoints. On-site safety measures such as fire extinguishers, breathing equipment, protective clothing, etc., were reviewed for adequacy. Additionally, all emergency procedures, process safety control, emergency bypass controls and monitoring equipment (both for personnel and environmental safety) were evaluated. At the culmination of the safety review, the team prepared a report detailing all findings and recommendations. The safety review report was evaluated by RTU project management and all necessary changes to plant operation, facilities, and procedures were made.

In parallel with the safety review, personnel training was conducted. This pre-start-up training effort had as its primary goal the safe and orderly operation of the RTU during start-up, run and shutdown sequences. To facilitate the achievement of that goal, all operating, laboratory and engineering personnel were familiarized with the appropriate procedures, both normal and emergency. The training consisted of both operating procedure study and on-site experience with the processing equipment and area to familiarize personnel with types and locations of processing equipment, valves, service facilities, instrumentation and control hardware, effluent monitoring equipment and emergency control points.

### 5.1.2 Shakedown Operations

A detailed shakedown plan was submitted to EPA in June 1977.(9) In general, that document described in detail the planned objectives, approach, sequences of operations, and expected results of the plant shakedown effort. The broad objectives of the RTU equipment shakedown period were as follows:

- Demonstration of equipment operability using coal and iron sulfate leach solution.
- Demonstration of the operability of the RTU at steady-state condition.
- Demonstration that controls, indicators and data acquisition systems were functional and suitable for repeated start-up, operation and shutdown sequences.
- Verification that sampling and analysis procedures were reproducible, safe and effective for the locations proposed, and that acceptable time delays between sampling and final result determinations were obtained.
- Estimation of the reproducibility of a single set of process conditions and the associated product characteristics.
- Standardization of settings of instruments, control devices and equipment to obtain desired ranges of pressure, temperature, volume, flowrate, weight, agitation rate, transfer rate, etc.
- Determination of the practical operational equipment limits for preparation and feeding of coal slurry, slurry flow and mixing and filtration operations.
- Demonstration that all RTU mechanical components and by-passes operated without unscheduled interruption or mechanical failure over the proposed operational ranges of flowrate, pressure, temperature and chemical environment.

The general approach to the shakedown of the RTU consisted of the sequential imposition of increasing numbers of stress-producing environments on the unit operations of the process. In this manner, identification and correction of any problems were expected. Also the gradual approach enabled personnel development of familiarity with process controls, checkout procedures, etc., in an easily assimilated manner. Each set of stress-producing environments was studied under continuous steady-state operation of the RTU over a period of time (hours), followed by inspection of the equipment and an assessment of its performance. The testing sequence which was followed during shakedown and the resultant accomplishments are summarized in Table 2. The table indicates the reactant media (i.e., coal type and size, liquid phase component, and gaseous phase component) and the primary activities carried out during each test run.

## TABLE 2. RTU SHAKEDOWN SEQUENCE

| Run No. | Coal Type | Reactant Media<br>Liquid Phase | Gas Phase | Major Accomplishments |
|---|---|---|---|---|
| 001 | None | Process Water | Nitrogen | System operated warm. System dynamically leak checked under nitrogen gas pressure. Foreign material flushed from system components. |
| 002 | Coal 1<br>14 mesh x 0<br>100 mesh x 0 | Distilled water (no added iron sulfate) | Nitrogen and oxygen | System operated hot. Initial coal feed operations and sampling procedures evaluated at two feed coal sizes. Effluent gas analysis equipment and procedures checked. Initial data acquisition system evaluated. Pumping capabilities verified. |
| 003/004* | Coal 1<br>14 mesh x 0 | Water (no added iron sulfate) | Nitrogen | Coal feed system operation and sampling verified. Reactor operated at maximum temperatures and gas pressures. Filter settings evaluated and filter cake samples obtained. Two shift operation attained. Initial mass balances obtained. Reactor wall and pump-around loop samples evaluated. Process sampling procedures and control lab analysis procedures evaluated. |
| 005 | Coal 1<br>14 mesh 1 0 | Water (no added iron sulfate) | Oxygen | Obtained baseline (no added iron salt) reaction data. Verified operability of instrumentation needed for mass balance. Evaluated mixer and reactor sampling (wall vs. loop) results and procedures. Verified coal analysis reproducibility. |
| 006 | Coal 1<br>14 mesh x 0 | Leach Solution (water plus added sulfuric acid and iron sulfate) | Oxygen | Verified proper mixer settings to effect efficient coal/leach solution wetting without foaming. Verified operating, sampling, and analysis procedures using leach solution. Obtained initial coal desulfurization data with leach solution. Regeneration rate evaluated. Filter operation evaluated with leach solution. |

* Test runs 003 and 004 were accomplished during one testing sequence.

As was expected, during shakedown operations, some equipment related difficulties were encountered. Those which resulted in significant equipment modifications and/or lengthy duration rework are summarized below.

- Turbine meters were initially installed in liquid flow monitoring service. During shakedown operations, most liquid circulating lines tended to build up in particulate loading (up to a few hundredths of a percent solids) due to the various recycle loops and the closed loops water system. The turbine meters were found to be inoperable when subjected to any degree of particulate loading. They were, therefore, replaced by magnetic flow meters which were capable of handling virtually any stream, from particulate free liquids to concentrated slurries.

- The Autoweigh weigh belt would not operate to the required ±0.5 percent accuracy as initially configured. This degree of accuracy was required in order to achieve a reasonably accurate mass balance around the system. Both hardware and electronic difficulties were encountered during the early shakedown period. Weigh belt internals and electronics were exchanged several times (by the manufacturer) for redesigned/modified replacements. Following supplier modifications, the unit was found to operate within the specified tolerance levels.

- Filter modifications were required after it was determined that back flooding of the belt (slurry back-up and overflow from the rear of the unit) occurred when trying to achieve maximum cake thicknesses or when belt slippage and momentary belt slowing occurred. This problem was solved by modifying the slurry feed distributor and by adding a dam at the rear of the belt.

- During the initial shakedown test, it was determined that the reactor feed pump P-1 (and its potential spare P-7) would not pump cold solution at the required pressure. This was found to be the result of internal pump rotor to stator tolerance levels. The close tolerance required to enable the pump to achieve high delivery pressures at the low flow rates and high temperatures required for reactor operations grew to an inoperable tolerance level when pump parts ran cool. This occurrence was the direct result of thermal expansion/contraction effects. The problem of cold feed pump inoperability was circumvented by revising procedures to include initial heat-up of the unit. This was accomplished via closed loop recirculation of heated (by direct steam injection) mix tank T-2 contents through P-1 and back to the mix tank. P-1 was usable in recirculating service because of the low head required to pump from P-1 back to T-2 as opposed to the high head required to pump against reactor R-1 pressures.

- Several hours into the initial leach solution run (Run 006), a major leach solution leak (acid spray) occurred which forced the system into an emergency shut-down. The plant was shut down and personnel evacuated the test stand within minutes of the incident. There were no injuries or equipment damage as the result of the rapid emergency procedure. The cause of the acid spary was found to be an improperly installed pipe flange on one of the leach solution supply lines. The flange was determined to be of carbon steel construction instead of the specified 316 Stainless Steel required for acid service. As a result of the incident, a thorough reinspection of the RTU was carried out to assure that all piping, flanges, and valves had been installed as specified. No other improperly installed equipment was discovered.
- Following evaluation of initial leach solution regeneration rate data, obtained during the first leach solution run, it was determined that insufficient solution regeneration in the reactor was occurring. This occurrence was thought to be the result of low turbulence experienced in the reactor pump-around loops where regenerant oxygen is blended with circulating slurry. To enhance regeneration and thereby increase coal desulfurization potential of the system, the oxygen blending portion of the recirculation loops were modified. The original 1-1/4 inch Schedule 80 pipe was replaced with 3/4-inch Schedule 40 pipe to increase flow velocities and therefore increase turbulence. It was determined in subsequent runs that reducing the pipe diameter did indeed increase regeneration rates to acceptable levels.

In summary, the RTU was operating successfully during the final phase of shakedown operations and most of the planned objectives of the overall effort were met. The various subsystems of the RTU were found to operate in an integrated fashion as anticipated. For instance, the three T-2 mixer stages were found to be maintainable at uniform temperature or with increasing temperature for each succeeding stage within the planned slurry flow rate ranges. Plant startup was accomplished over an approximate 3-4 hour period, which was deemed adequate to meet the objectives of the operational test plan. Reactor temperatures were demonstrated controllable up to 275°F using the available steam source, and a fully burdened system, including heat exchangers, belt filter, mixer and reactor. The reactor pressurization and control system performed as expected. The nitrogen, air, and water supply systems were of adequate capacity and controllability for all purposes intended. The coal and slurry transfer systems functioned satisfactorily, as desired, following equipment modifications. The belt filter performed as intended up to a maximum slurry feed rate of 1500 pounds per hour. Beyond that limit, belt flooding and incomplete filtration was found to occur. An acceptable leach solution regeneration rate was attained following modifications.

The objectives of the concurrent support activities were also met during shakedown activities. All data generated during shakedown was evaluated with acquisition hardware and software being modified and/or generated where appropriate. Suitable data recording formats were developed which allowed for fast and accurate data retrieval. The data itself was evaluated primarily to determine baseline process chemistry. In the control laboratory, procedures were verified and techniques developed which proved to yield accurate and reproducible laboratory analysis data. At the conclusion of shakedown, a revised Operational Test Plan(10) was generated and submitted to EPA. The plan was revised in the context of the newly acquired data on a working knowledge of the processing equipment operating limitations and capabilities. The submission of that document signaled the end of RTU shakedown operations.

## 5.2 RTU OPERATION

The RTU was brought into operational status immediately following shakedown activities. During the course of operations, it was demonstrated that the RTU could be operated continuously to test Meyers Process units for coal-leach solution mixing, simultaneous coal depyritization and leach solution regeneration, filtration of leach solution from treated coal, and product coal water washing. No difficulties were encountered in changing process variables such as coal feed rates, leach solution feed rates, steam flow rates, reactor pressure, oxygen flow rates, agitation and/or pump-around rates, or filter conditions during RTU operations. Sixteen distinct sets of operational variables were systematically studied while treating 49,700 pounds of coal over a total operating period of 254 hours. Many of the variable changes were made during continuous elongated run sequences, up to 32 hours in duration, demonstrating the overall flexibility and controllability of the RTU.

### 5.2.1 Operating Procedures

Prior to initiation of the planned experimental testing effort, the RTU operational procedures were reviewed and revised in light of the previously acquired shakedown experience. Those procedures are tabulated by name and identification number in Volume II, Appendix B of this report. The following paragraphs describe the nominal start-up, operating and shut-down sequences followed during operation of the RTU.

Prior to RTU start-up, all auxiliary supply systems are activated. It is the auxiliary supply systems which provide nitrogen, oxygen, utility/instrument air, leach solution and process/cooling water to the RTU. Nitrogen is used primarily as a purge gas in the coal feed and reaction systems. Oxygen is employed for reagent regeneration in the primary reactor and, with minor piping modifications, could be utilized in the secondary reactor also. Air is used to drive equipment (i.e., pumps P-8 and P-11) and to actuate various plant instrumentation. Start-up of auxiliary supply systems consists primarily of verifying all associated valve and regulator settings, verifying the adequacy of material supplies, and subsequent supply initiation. Once these supporting systems have been activated, RTU start-up procedures are initiated.

RTU start-up procedures may be summarized by processing unit. The first step in start-up of all units is verification of associated instrumentation. Prior to start-up of the coal feed system, the coal level in storage tank T-1 is verified to be sufficient for test initiation or, if needed. additional coal is transferred from tote bins to T-1. The storage tank T-1, weigh belt A-3 and rotory valve A-4 are purged with nitrogen and then activated. Start-up of the mixer T-2 includes verification of weir heights and initiation of mixing with M-1 through M-3. Steam flow to T-2 is initiated and slurry pump P-1 is activated in a recirculation mode to stage three of T-2; slurry recirculation is maintained until the P-1 effluent temperature exceeds 200°F. Start-up of the primary reactor R-1 requires verification of seal flush water flow, initiation of slurry recirculation through pumps P-2 through P-6, and activation and regulation of the R-1 pressure relief valve PIC-43. Mixers M-4 through M-8 are turned on to augment agitation provided by the slurry recirculation loops. Steam and gas (either nitrogen, oxygen or a mixture thereof) flows to R-1 are initiated after verification of PIC-43. Activation of the belt filter S-1 is preceded by verification of all filter valving and activation of the vacuum pump K-1 and reagent filtrate and wash filtrate pumps P-9 and P-10. S-1 belt speeds are adjusted to a nominal setting and coal cake steaming and wash streams are activated. Processed coal catch bins are positioned prior to initiation of filtration.

Upon pressurization of R-1 and heat up of P-1, slurry flow through the RTU may be initiated. The coal discharge vibrator A-2 is activated and coal is fed to A-3 and, subsequently, to T-2. Reagent feed pump P-13 is turned on providing hot reagent to T-2 through V-1 and T-3. Reactor effluent slurry flow rates through P-1 and KV-241 (R-1 slurry vent valve) are adjusted to maintain desired slurry levels in T-2 and R-1. Filter belt speeds are adjusted at this time to yield a properly dewatered processed coal filter cake. Procedures for plant operation after steady slurry and gas flows have been obtained consist largely of control adjustments to maintain specified reaction temperatures, pressures, flow rates and slurry levels. The complete start-up operation requires approximately 4 to 6 hours, depending primarily on the steady state reactor temperature desired.

Plant shut-down is initiated by terminating all RTU feed and transfer streams including coal, reagent, slurry, gas and steam. Recirculation pumps are shut off and the R-1 unit is depressurized. Belt filter operation proceeds until coal is no longer discharged into the catch bins and then S-1 operation is terminated. All vacuum and filtrate pumps are subsequently shut off. The T-2 and R-1 mixers are left operating to prohibit retained slurry settling. After the RTU has been secured, all slurry transfer pumps (including recirculation pumps) and piping are drained and flushed with clear water. The final step in the RTU shut-down sequence is shut-down, venting and securing of the auxiliary supply systems. The entire shut-down sequence requires approximately 2 hours to accomplish. The heated slurries contained within the mixer T-2 and reactor R-1 require an additional eight to ten hours to cool to ambient temperatures.

### 5.2.2 Equipment Experience

During the 4-month operational test phase of the project, 16 discrete tests were conducted. The specific test sequences and related processing conditions over which the RTU was operated are delineated in Section 8. A summary of the major equipment operational ranges utilized while carrying out the experimental test sequences is presented in Table 3. In general, the equipment performed well within the limits studied. There are, of course, several observations relating to equipment operating experience worth noting.

## TABLE 3. EQUIPMENT RANGES UTILIZED

| Equipment | Service | Range Utilized During Operational Testing |
|---|---|---|
| Weigh Belt A-3 | Coal Feed | 199 - 300 lbs/hr |
| Mixer T-2 | Coal - Leach Solution | 156°- 215 °F<br>1.1 - 1.8 hrs residence time |
| Reactor R-1 | Coal - Leach Solution - $O_2$ | 199°- 273 °F<br>23 - 80 PSIG<br>5.1 - 8.2 hrs residence time<br>58 - 141 SCFH $O_2$ |
| Pumps P-1, P-7 | Slurry Feed Pumps | .8 - 4.2 gpm<br>23 - 80 PSI ΔP |
| P-2/6 | Slurry Circulation Pumps | 18 - 25 gpm |
| P-8 | Belt Wash Pump | 0 -- 2 gpm |
| P-9 | Filtrate Pump | .6 - 4.6 gpm |
| P-10 | Wash Pump | 1.1 - 2.0 gpm |
| P-11 | T-6 Discharge Pump | Not Used |
| P-12 | Leach Solution Pump | 1 - 20 gpm |
| P-13 | Leach Solution Feed Pump | 1.2 - 3.0 gpm<br>23 - 80 PSI ΔP |
| P-14 | Waste Disposal Pump | 200 gpm |
| P-15 | Cooling Water Pump | 100 gpm |
| P-16 | Seal Water Pump | 12 gpm |
| Mixers M-1/3 | Mix Tank Mixers | 150 - 200 RPM |
| M-4/8 | Reactor Mixers | 150 - 200 RPM |

Coal Feed Equipment. The coal transfer equipment performed well for coal feed rates up to 300 pounds per hour. A minor modification to the weigh belt unit was required to accommodate accidental coal spillage and dusting over belt edges. The modification consisted of the addition of a dust collection chute and flanged discharge port underneath the belt compartment. This modification allowed quick periodic removal of coal particulate buildup. A second intermittant situation requiring equipment modification occurred in this section of the RTU. The dry coal delivery chute to the mixer T-2 occasionally plugged, requiring short duration recirculation mode operation of T-2 while the plug was dissipated either by external chute tamping or chute disassembly and unplugging. The cause of this occurrence was found to be steam backflow from the first stage of the mixer (which was normally operated at 185° to 190°F) which resulted in coal wetting and agglomeration. The situation was circumvented by reducing nominal first-stage mixer temperatures to 170°F, by increasing nitrogen downflow through the chute, and by installing a cooling coil to the outside of the chute.

Leach Solution Feed Equipment. The leach solution feed equipment, including the solution storage tanks T-7 and T-8, heat exchanger E-2, knock-out drum V-1, associated piping, valves, control and instrumentation, performed reliably during operation. There was, however, some difficulty experienced with the leach solution feed pump P-13. Midway through operational testing, several outer shaft seal failures were experienced in rapid succession. Following thorough disassembly and inspection of pump internals, it was determined that the pump contained a small inner connecting shaft of carbon steel construction. It had been installed in the unit during pump manufacture. The inner shaft had corroded and resulted in an inner shaft seal failure which allowed the acidic leach solution to attack the main outer seals. A replacement of inner shaft 316L was fabricated and installed in P-13. Also, near the end of operations a P-13 rotor related problem was experienced. The problem was manifested as an inability of the pump to meet desired throughputs at operating pressures. It was determined upon inspection of pump internals, that the chrome plated 316L rotor had crazed and that the chrome plating had flaked off, thus resulting in too great a clearance between the pump rotor and stator. This oversize clearance allowed backflow of the leach solution and therefore limited pumping ability. In order to minimize plant down time, the P-13 rotor was replated with chrome and placed back into service. The rechromed rotor was still in service at the conclusion of operations. A new 316L stainless steel rotor (not chrome plated) was fabricated and is currently warehoused as a future replacement spare.

Mixing Equipment. The coal mixing equipment, consisting of mix tank T-2, mixers M-1 through M-3, foam knock-out unit T-3, and all associated hardware performed as expected with the exception of the steam inlet lines to T-2. Early in operations, the lines were found to clog with coal particulate and leach solution which had backflowed from T-2 during unit shut-down and cooling. The apparent cause of the backflow was steam collapse in the lines upon cooling combined with faulty check valves in the inlet lines. The check valves were replaced and a steam venting sequence was added to the shut-down procedures. Another observation worth noting is that there were no instances of foaming in T-2 during the entire operational phase of the project.

Reactor Equipment. For the most part, the equipment associated with the reactor R-1 performed as expected. The slurry circulating pumps P-2 through P-6, the reactor mixers M-4 through M-8, the knock-out drum T-5, the oxygen and nitrogen systems, the temperature, pressure and level control systems, and associated instrumentation performed satisfactorily. The slurry feed pump P-1 (and its spare P-7) experienced the same difficulties as experienced by the leach solution feed pump P-13 (discussed in preceding paragraphs) at the conclusion of operations. In addition to the flaking and seal problems, the 316L pump rotor also experienced corrosion and/or errosion. The unit lost pumping capability as was the case with P-13. The additional corrosion/erosion factor was believed to be the result of the abrasive nature of the coal containing slurry as feed to R-1 as opposed to the leach solution liquid handled by P-13. As in the case of P-13, the reactor feed pump P-1 (and P-7) was replated with chrome to the specified tolerance limit and put back into service to minimize RTU down time. The pump ran satisfactorily for several hours prior to chrome plate flaking followed by pump failure. Following the second failure it was determined that the thicker chrome plating (required to make up for corrosion/erosion loss) was unable to withstand the thermal expansion experienced during plant start-up. A new Hastelloy C-276 rotor was fabricated and installed in P-1. The selection of Hastelloy C-276 was based on RTU corrosion studies (discussed in Section 10) and pump manufacturer recommendations.

The R-1 ball valve slurry sampling system was found to operate satisfactorily. Both wall and pump-around loop sampling equipment obtained representative and reproducible R-1 slurry samples (discussed in Section 8). Therefore, early in the testing sequence, circulation loop sampling was terminated due to a tendency for those sample outlets to clog during use. The direct introduction of steam into R-1 to maintain desired reactor temperatures was found to dilute the recycled leach solution over prolonged running periods. An appreciable part of the dilution was due to repeated plant start-ups (the plant was not operated over weekends, and was shut down during planned maintenance and repairs). This dilution factor would be less, were the RTU in a continuous operation mode. However, reactor leach solution regeneration capability was sufficient to maintain adequately concentrated ferric reagent supply throughout operation, despite the dilution effect.

The reactor associated equipment which was subjected to elevated temperature (>215°F) and oxygen partial pressure operation did experience a systematic corrosion related problem (discussed in detail in Section 10). During the course of operations, the reactor R-1, reactor internals, and slurry circulation loop piping experienced progressively severe corrosion. The reactor and its internals experienced pitting and crevice corrosion. The pump-around loops experienced crevice corrosion at flange interfaces and pitting. The damage to the reactor and loop piping/flanges was sufficiently severe by mid-operations to warrant reactor repair (filling of the deeper pits with weld rod material) and replacement of reactor associated piping with new 316L material. At conclusion of operations, following unit inspection, the reactor and its associated piping were again found to have experienced severe pitting corrosion. Based on the RTU materials study effort (detailed in Section 10), it has been determined that a new reactor and associated piping, flanges and valves should be constructed and put into service prior to further RTU operation. Based on the corrosion study, the new reactor and piping, flanges and valves should be of titanium construction. This construction material is predicated not only by material study results but also by the size of the equipment (the reactor and piping are too small in size to be applicable to metallic and/or nonmetallic liners and/or acid brick lining) and the relatively low cost of titanium replacement parts. For instance, a quote of $49,300 was obtained in January 1978 for a replacement reactor of titanium construction, as compared to $25,900 which was paid for the original 316L reactor in early 1976.

Filtration Equipment. The filtration equipment, including the belt filter S-1, the belt wash return pump P-8, the filtrate receiver V-2, the filtrate pump P-9, the wash receiver V-3, the wash pump P-10, and the filter vacuum pump performed as expected. The belt filter control variables (wash water temperature, flow rate, belt speed, wash location, vacuum level, etc.) were such that adequate filtration and washing of 14 mesh x 0 coal was attained up to a total slurry feed limit of 1500 pounds per hour. The belt filter therefore became the capacity limiting unit in the RTU. Belt blinding did not occur to an appreciable extent. However, the filter belt did fail (it was literally ripped apart) at one point in the test program. Belt failure was attributed to a softening of the belt rubber facing primarily as a result of prolonged elevated temperature (180° to 190°F) exposure to acidic slurry feed. The belt, as a result of the softening, experienced increased frictional forces at the belt interface to the unit vacuum pans. Following belt failure, the belt was repaired and placed back into service. The vacuum pan edges over which the rubber belt travels were fitted with teflon overlays. The teflon-belt interface resulted in less system frictional forces, thus allowing proper belt operation for the duration of operations.

## 5.3 RTU OPERATION CONCLUSIONS

1. Pre-start-up RTU safety reviews and personnel training were successfully completed.
2. Shakedown activities demonstrated equipment operability, and equipment functionality over the desired test ranges.
3. Shakedown activities verified RTU sampling and analysis procedures and resulted in the acquisition of baseline process chemistry data.
4. RTU operating procedures were modified prior to RTU operations in the context of shakedown derived experience.
5. A revised RTU Operational Test Plan was generated based on information obtained during shakedown.

6. During RTU operations, 49,700 pounds of coal were treated over a total of 254 hours.

7. Continuous RTU operation was demonstrated for periods up to 32 hours in duration.

8. Sixteen distinct sets of operational variables were studied.

9. RTU controllability and flexibility was demonstrated.

10. Sufficient data was obtained during operations to allow process chemistry evaluation and verification.

11. Most of the RTU equipment performed as expected without incident.

12. Some RTU equipment experienced operating difficulties but in general modification to the affected equipment and/or procedural changes resulted in acceptable unit operation.

13. Elevated temperature operation as experienced in the reactor section of the RTU resulted in unexpectedly severe corrosion to equipment and piping internals.

14. The reactor R-1 and its associated piping, flanges and valves need to be replaced prior to further RTU operation.

# 6. REACTOR TEST UNIT DATA

## 6.1 SUMMARY OF PREVIOUS BENCH SCALE EXPERIMENTATION

Meyers Process chemistry has been characterized through bench scale experimentation consisting of more than 200 mass balanced experiments. These tests were performed primarily with Appalachian coals(4,5,11) although coals from the Interior Basin and Western regions have also been tested(1,4). The resultant data compilation shows that the pyrite leaching and reagent regeneration steps of the Meyers Process may be expressed as follows:

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \rightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8\ S$$

and

$$2.3\ O_2 + 9.2\ FeSO_4 + 4.6\ H_2SO_4 \rightarrow 4.6\ Fe_2(SO_4)_3 + 4.6\ H_2O.$$

Pyrite leach reaction products were initially determined by direct measurement of sulfate sulfur and elemental sulfur generated during ferric chloride leaching. Multi-stage toluene extractions were utilized to ensure complete elemental sulfur recovery from processed coals. Sulfur balances generally indicated better than 95% sulfur recovery and further verified the measured product sulfur ratios. Later experimentation performed with ferric sulfate reagent also verified preliminary findings through measurement of pyrite removals and recovered elemental sulfur. Thus it was determined that each mole of pyrite reacted yields 1.2 moles of reagent soluble sulfate sulfur ($FeSO_4$ and $H_2SO_4$) and 0.8 moles of elemental sulfur. This product sulfate sulfur-to-elemental sulfur ratio of 1.5 was found to be independent of the following processing variables: 1) reaction temperature up to 270°F, 2) reagent anion (sulfate or chloride), 3) reagent acidity down to a pH of 1, 4) reagent total from concentration to approximately 10% w/w and 5) oxygen partial pressures to 85 psia.

It should be noted that losses or incomplete extraction of elemental sulfur will result in an apparent product ratio which is greater than 1.5. For this reason, bench scale data obtained using single stage toluene extractions tend to indicate slightly high product ratios.

Pyrite leaching and reagent regeneration reactions have been found to proceed at rates which are expressed by the following empirical equations:

$$r_L = \frac{-dW_p}{dt} = K_L Y^2 W_p^{\,2}$$

where

| | |
|---|---|
| $K_L$ | is the pyrite leach reaction rate constant |
| $Y$ | is the ratio of reagent ferric ion-to-total iron concentration |
| $W_p$ | is the weight percent of pyrite in coal |

and

$$r_R = \frac{-dFe^{+2}}{dt} = K_R P_{O_2} (Fe^{+2})^2$$

where

| | |
|---|---|
| $K_R$ | is the reagent regeneration rate constant |
| $P_{O_2}$ | is the oxygen partial pressure |
| $Fe^{+2}$ | is the reagent ferrous ion concentration. |

Rate constants for the pyrite leaching and reagent regeneration reactions, $K_L$ and $K_R$, have an Arrhenius type exponential temperature dependence which is expressed as:

$$K = A \exp\,[-E/RT]$$

where

| | |
|---|---|
| A | is the pre-exponential or frequency factor |
| E | is the apparent overall activation energy |

R     is the gas constant and

T     is the reaction temperature.

The pyrite leach reaction frequency factor $A_L$ is a function of coal type and coal particle size distribution. The value of $A_L$ increases with decreasing coal particle size distribution for a specified coal. For Lower Kittanning coals such as that from the Martinka mine, the value of $A_L$ obtained from 14 mesh top-size coal samples ranges from approximately $3 \times 10^5$ $W_p^{-1}$ hour$^{-1}$ to $7 \times 10^5$ $W_p^{-1}$ hour$^{-1}$. The value of $A_L$ may be increased either by size reduction of the coal or by physical coal cleaning. Enhancement of $A_L$ by physical coal cleaning may be attributed to the removal of coal particles containing pyrite having a low specific surface area or low accessibility (isolation by the matrix material). Thus, pyrite removal rates may be increased by coal size reduction and/or physical cleaning.

An apparent activation energy for the pyrite leach reaction $E_L$ of approximately 11.1 kilocalories per mole of pyrite reacted was determined from bench scale experimentation. Hence, the pyrite leach reaction is strongly temperature dependent with reaction rates nearly doubling for each $36^{\circ}$F temperature increment in the temperature range investigated. However, the reaction rate temperature dependence has been observed to vanish after 80-90% pyrite removal from some high pyrite ROM Lower Kittanning coals. This observation appeared to indicate that pyrite leach rates can become diffusion limited and thus, rather insensitive to temperature changes.

The reagent regeneration rate constant $K_R$ is a function of the regeneration pre-exponential factor $A_R$, apparent activation energy $E_R$ and reaction temperature. The value of $A_R$ is dependent on the efficiency with which oxygen and reagent are contacted. That is $A_R$ contains an efficiency factor (i.e., $A_R = \epsilon A_R'$) which relates to the effective reagent-oxygen contact area and contact time. The efficiency factor $\epsilon$ of a specified regeneration apparatus may have a slight temperature dependence since solution viscosity and specific volume are temperature dependent. However, within the temperature range investigated temperature effects upon $\epsilon$ are considered to be small. During bench scale experimentation, values of $A_R$ up to $6.7 \times 10^5$ liters/mole-atmosphere-minute were obtained. Since larger values of $A_R$ were not attainable at bench scale, this value is assumed to correspond to an efficiency factor of unity. The value of $E_R$ was found to be a constant 13.2 kilocalories per mole of $Fe^{+2}$ oxidized.

Pyrite leach rates are proportional to the square of reagent Y. Thus a high ratio of ferric ion-to-total iron must be maintained during processing to maximize pyrite leach rates. In order to maintain high reagent Y values during processing with low iron reagent or during processing with high solids content slurries, reagent regeneration may be performed simultaneously with the leach reaction. Bench scale tests have demonstrated that reagent Y values and pyrite leach rates are increased by simultaneous leach-regeneration (L-R) processing with no apparent adverse affect on regeneration efficiency. Further, L-R processing has not been found to affect the product sulfate sulfur-to-elemental sulfur ratio.

Selectivity of ferric sulfate toward the oxidation of coal pyrite has been verified by measurements of excess ion consumption and by measurements of mineral matter free (mmf) coal heat content changes. The extent of both excess ferric ion consumption and mmf heat content degradation have been found to decrease with increasing coal rank. Bituminous coals of Appalachia may show approximately 1% decrease in mmf coal heat content (very nearly the limit of analytical precision) as a result of Meyers processing at 212°F while the mmf heat content of Western sub-bituminous coals has shown an average decrease of nearly 7% under identical processing conditions. Bench scale experimentation performed with 14 mesh x 0 mine cleaned Martinka coal and acidified iron sulfate reagent indicated an mmf heat content decrease of less than 1% for up to 48 hours of 212°F processing, although L-R processing at 250°F for 6 hours or more resulted in an mmf heat content decrease of approximately 2%(11). Thus, it appears that selectivity of the iron sulfate reaction with pyrite may decrease somewhat with increasing reaction temperature and/or increasing oxygen partial pressure.

Further verification of leach reaction selectivity was provided by material balance data which, for Lower Kittanning coals processed at temperatures of 212°F to 250°F with 0 to 5% w/w iron reagents, indicated virtually complete solids recovery with a balance precision of approximately 2%.

Product sulfate sulfur and elemental sulfur are generally recovered from Meyers Process leached coal by water washing and subsequent solvent extraction or vaporization. The sulfate sulfur product is readily dissolved in the reagent solution and may be recovered from recycled reagent slip-streams either by liming or by a combination of liming and evaporative concentration of reagent to precipitate ferrous sulfate. Elemental sulfur recovery can be effected by solvent extraction with numerous solvents which are non-reactive with sulfur at moderate temperatures including toluene, acetone and hexane. Toluene has been most commonly used for routine laboratory extractions. Bench scale extraction experimentation performed with 14 mesh x 0 mine cleaned Martinka coal shows approximately 97% elemental sulfur recovery with a single stage toluene extraction. Acetone has also been demonstrated to be an effective sulfur extraction solvent which, unlike toluene, is completely miscible with water and can therefore be utilized in conjunction with coal washing. As such, acetone may be preferable to toluene for large scale extraction applications. Alternate approaches to elemental sulfur recovery include techniques involving vaporization into an inert gas stream and sulfur recovery by vacuum distillation. However, vaporization techniques were not employed during the RTU program.

Specific details of previous bench scale experimentation as they apply to the RTU program are presented in the ensuing data reduction sections.

## 6.2 DATA FROM THE REACTOR TEST UNIT

Operation of the RTU was continuously monitored and recorded either by the Doric data logger or manually. Primary data sources, those which required monitoring for plant operation or evaluation of the Meyers Process kinetics, were recorded by the data logger on magnetic tapes. These tapes were shipped to Space Park where they were converted by computer program from the Doric format to engineering formats. Secondary data from the RTU (i.e., flow rates not critical to plant operation or kinetic evaluation) were monitored and recorded manually. Analytical data relating to slurry and coal analyses were also recorded manually although the raw data was processed through computer programs to yield the various analytical results in selected formats. Computer programs developed for data treatment during this program are presented in Volume II, Appendix A.

Magnetic tapes generated by the Doric data logger are capable of storing data from 99 channels plus one self-check channel. At the conclusion of the program, 49 channels were in use to record numerical data and 28 channels were in service as indicators (alarm channels). Remaining channels were available for allocation as required. Data stored on these tapes were converted from the Doric format to two engineering formats which are presented in Tables 4 and 5. The format presented in Table 4 represents a scan of all channels in use at the time indicated by the heading (Julian day, hour:minute:second) and is essentially self-explanatory. Only active channels are displayed. The Ramapo excitation monitor (Channel 40) is used as a panel-mounted voltmeter which facilitates calibration checks of the R-1 feed and vent oxygen streams, Fe-61 and Fe-44. The transducer pressure sensor monitor (Channel 99) serves a similar function with regard to pressure measurement equipment. The format presented in Table 5 provides all the data taken for each channel during a specified experimental period. The latter format is somewhat more abbreviated than that presented in Table 4 and improves the ease of data evaluation and interpretation in terms of identifying trends. Thus, the format presented in Table 5 was used most frequently.

After conversion of the magnetic tape contents to engineering units, the data were available in storage for use in any of various computer programs prepared during this project to facilitate data reduction (i.e., plotting, averaging, mass balances, rate determinations, etc.). Similarly, all control lab analytical data in storage was available for recall into the data reduction programs. Manually recorded pilot plant data required as input for data reduction programs were input to central data storage through the computer terminals or, for large inputs, were submitted as a keypunch card deck. Thus, nearly all data obtained from the RTU was centrally stored and readily available for recall. Only those manually recorded data relating solely to plant operation were not included in the centralized data compilation.

A complete file of the raw data obtained from the RTU facility is stored at TRW. Data which are pertinent to process evaluation are presented in the ensuing subsections of Section 6.

TABLE 4. RTU CHANNEL-SCAN AT FIXED TIME

```
RUN 03-03-00     DAY  10      9:39:00
CHANNEL  PARAMETER              TAG           DATA   UNITS          ALARM
    0    SELF CHECK             UJR-170      4.999   VOLTS
    1    T-2 CELL 1 TEMP        TE-19        135.7   DEG F
    2    T-2 CELL 2 TEMP        TE-20        134.3   DEG F
    3    T-2 CELL 3 TEMP        TE-21        127.0   DEG F
    4    R-1 CELL 1 TEMP        TE-52        212.3   DEG F
    5    R-1 CELL 2 TEMP        TE-53        202.5   DEG F
    6    R-1 CELL 3 TEMP        TE-54        205.4   DEG F
    7    R-1 CELL 4 TEMP        TE-55        206.2   DEG F
    8    R-1 CELL 5 TEMP        TE-56        205.7   DEG F
    9    OXYGEN TEMP TO R-1     TE-173        55.0   DEG F
   10    V-1 DISCH GAS TEMP     TE-145        55.0   DEG F
   11    LEACH TO V-1 TEMP      TE-199        59.5   DEG F
   12    LEACH FROM V-1 TEMP    TE-200        71.6   DEG F
   13    R-2 TEMP               TE-99         56.1   DEG F
   15    OXYGEN FLOW TO R-1     FE-61          4.1   SCFM
   16    V-1 DISCH GAS FLOW     FE-44          0.0   SCFM
   17    O2 ANAL REFERENCE      A -171       98.61   PERCENT
   18    O2 ANAL SAMPLE         AE-171       90.15   PERCENT
   19    AUTOWEIGH TOTAL        WT-9      5661       POUNDS
   20    AUTOWEIGH RATE         WT-9A          -.2   POUNDS/HR
   21    R-1 PRESSURE           PT-173      -37.50   PSIG
   22    OXYGEN TO R-1          PT-172         0.0   PSIG
   23    V-1 DISCH GAS PRESS    PT-150        21.8   PSIG
   24    P-1 DISCHARGE FLOW     FE-79         .920   GPM
   25    P-2 DISCHARGE FLOW     FE-83         .869   GPM
   26    P-3 DISCHARGE FLOW     FE-84         .674   GPM
   27    P-4 DISCHARGE FLOW     FE-85        1.842   GPM
   28    P-5 DISCHARGE FLOW     FE-86         .465   GPM
   29    P-6 DISCHARGE FLOW     FE-87        -.077   GPM
   30    T-3 LEACH FLOW         FE-31        -.014   GPM
   31    P-9 DISCHARGE FLOW     FE-157        .006   GPM
   32    P-10 DISCHARGE FLOW    FE-158        .005   GPM
   33    P-7 DISCHARGE FLOW     FE-101      -1.250   GPM
   34    T-2 SLURRY LEVEL       PT-26         13.3   INCHES
   35    R-1 SLURRY LEVEL       PT-58         11.0   INCHES         LOWER
   36    PUMP P-1 DISCH PRESS   PT-29       -50.00   PSIG
   37    H2 SUPPLY TO R-1       PT-307       60.10   PSIG
   38    S-1 VACUUM PAN A       PT-249      14.560   PSIA
   39    S-1 VACUUM PAN B       PT-250      -3.750   PSIA
   40    RAMAPO FX. MONITOR                 -0.000   VOLTS
   41    LEACH SL TEMP TO T-3   TE-32         56.5   DEG F
   42    T-4 TANK TEMP          TE-201        65.1   DEG F
   43    V-1 TANK TEMP          TE-202        60.0   DEG F
   44    T-4 H2O IN TEMP        TE-203        68.6   DEG F
   45    T-10 FLUSH H2O TEMP    TE-195        69.2   DEG F
   46    P-1 DISCH TEMP         TE-28         77.3   DEG F
   47    S1 INLET TEMP SLURRY   TE-           58.7   DEG F
   48    T-4 H2O OUT TEMP       TE-204        68.2   DEG F
   90    PUMP P-7 DISCH PRESS   PT-100       -7.96   PSIG
   91    R-2 LIQUID LEVEL       PT-95         22.3   INCHES         LOWER
   99    XDUCER P.S. MONITOR                14.781   MV
```

# TABLE 5. RTU TIME-SCAN BY CHANNEL

| | | CHANNEL | CHANNEL | CHANNEL | CHANNEL | CHANNEL | CHANNEL | CHANNEL | CHANNEL | CHANNEL | CHANNEL | CHANNEL | CHANNEL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RUN | 03-03-00 | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| DAY | TIME | UJR-170 | TE-19 | TE-20 | TE-21 | TE-52 | TE-53 | TE-54 | TE-55 | TE-56 | TE-173 | TE-148 | TE-199 |
| 10 | 1:23:00 | 4.999 | 156.5 | 207.9 | 213.9 | 235.9 | 230.0 | 236.7 | 237.5 | 240.4 | 62.6 | 57.6 | 59.3 |
| 10 | 1:26:00 | 4.999 | 159.8 | 205.1 | 213.8 | 234.5 | 229.1 | 235.4 | 237.5 | 240.1 | 62.2 | 57.8 | 59.7 |
| 10 | 1:29:00 | 4.999 | 159.5 | 200.7 | 213.8 | 233.5 | 229.3 | 235.0 | 236.8 | 238.9 | 62.1 | 57.8 | 59.3 |
| 10 | 1:32:00 | 4.999 | 158.1 | 204.4 | 213.6 | 233.4 | 228.8 | 234.3 | 236.4 | 238.2 | 61.9 | 57.8 | 59.2 |
| 10 | 1:35:00 | 4.999 | 157.8 | 209.4 | 213.8 | 231.7 | 228.3 | 233.7 | 236.0 | 237.4 | 61.9 | 57.4 | 59.2 |
| 10 | 1:38:00 | 4.999 | 159.3 | 211.2 | 214.0 | 231.5 | 227.7 | 232.9 | 235.5 | 236.6 | 61.9 | 57.3 | 59.4 |
| 10 | 1:41:00 | 4.999 | 161.3 | 210.1 | 213.9 | 230.3 | 227.2 | 232.1 | 234.9 | 235.9 | 61.9 | 57.4 | 59.3 |
| 10 | 1:44:00 | 4.999 | 163.9 | 211.2 | 213.9 | 228.7 | 226.0 | 231.1 | 234.5 | 235.6 | 61.8 | 57.9 | 59.5 |
| 10 | 1:47:00 | 4.999 | 166.2 | 209.8 | 213.7 | 226.6 | 225.9 | 230.4 | 233.1 | 235.0 | 62.1 | 57.5 | 59.4 |
| 10 | 1:50:00 | 4.999 | 166.8 | 207.2 | 213.8 | 226.1 | 225.5 | 229.7 | 232.5 | 234.5 | 61.7 | 57.9 | 59.8 |
| 10 | 1:53:00 | 4.999 | 166.2 | 205.5 | 213.8 | 226.3 | 224.9 | 229.6 | 231.8 | 233.2 | 61.8 | 57.7 | 59.4 |
| 10 | 1:56:00 | 4.999 | 166.0 | 206.5 | 213.8 | 223.4 | 224.2 | 228.5 | 231.7 | 233.0 | 61.6 | 57.6 | 59.4 |
| 10 | 1:59:00 | 4.999 | 165.0 | 204.7 | 213.7 | 223.2 | 223.8 | 228.4 | 230.8 | 232.0 | 61.8 | 57.8 | 59.3 |
| 10 | 2:02:00 | 4.999 | 164.8 | 203.6 | 213.7 | 223.9 | 223.0 | 227.2 | 230.0 | 231.2 | 61.6 | 57.7 | 59.2 |
| 10 | 2:05:00 | 4.999 | 164.4 | 203.5 | 213.7 | 224.6 | 222.1 | 226.8 | 229.6 | 230.9 | 61.4 | 58.2 | 59.6 |
| 10 | 2:08:00 | 4.999 | 163.9 | 202.9 | 213.4 | 223.5 | 221.6 | 226.7 | 229.1 | 229.8 | 61.4 | 57.8 | 59.1 |
| 10 | 2:11:00 | 4.999 | 163.0 | 203.0 | 213.4 | 222.0 | 221.0 | 226.8 | 229.1 | 234.3 | 61.4 | 58.2 | 59.7 |
| 10 | 2:14:00 | 4.999 | 162.6 | 208.8 | 213.6 | 224.0 | 220.8 | 230.2 | 228.4 | 229.0 | 61.3 | 58.2 | 59.2 |
| 10 | 2:17:00 | 4.999 | 163.0 | 210.1 | 213.9 | 221.5 | 221.1 | 233.8 | 228.1 | 228.6 | 62.1 | 58.1 | 59.0 |
| 10 | 2:20:00 | 4.999 | 164.6 | 208.9 | 213.8 | 219.7 | 221.0 | 236.3 | 228.5 | 228.2 | 61.1 | 57.6 | 59.4 |
| 10 | 2:23:00 | 4.999 | 165.4 | 204.3 | 213.8 | 219.7 | 220.5 | 238.7 | 228.9 | 227.3 | 60.6 | 57.7 | 58.8 |
| 10 | 2:26:00 | 4.999 | 164.9 | 202.4 | 213.6 | 219.5 | 221.2 | 240.6 | 229.3 | 228.7 | 60.6 | 58.0 | 59.4 |
| 10 | 2:29:00 | 4.999 | 163.4 | 205.7 | 213.5 | 219.9 | 221.4 | 241.9 | 230.3 | 236.1 | 60.4 | 58.0 | 59.5 |
| 10 | 2:32:00 | 4.999 | 162.2 | 208.1 | 213.8 | 219.9 | 221.1 | 241.6 | 230.9 | 238.5 | 60.3 | 57.4 | 59.2 |
| 10 | 2:35:00 | 4.999 | 163.0 | 210.8 | 213.8 | 219.2 | 221.0 | 238.7 | 231.5 | 237.2 | 60.2 | 57.4 | 59.4 |
| 10 | 2:38:00 | 4.999 | 164.4 | 211.6 | 214.0 | 215.5 | 221.5 | 236.9 | 231.6 | 236.1 | 60.3 | 57.6 | 58.7 |
| 10 | 2:41:00 | 4.999 | 166.2 | 212.9 | 213.9 | 217.3 | 221.2 | 234.5 | 232.4 | 235.7 | 60.2 | 57.8 | 59.4 |
| 10 | 2:44:00 | 4.999 | 167.8 | 213.2 | 214.0 | 219.2 | 220.3 | 233.3 | 232.0 | 234.4 | 60.2 | 57.8 | 59.4 |
| 10 | 2:47:00 | 4.999 | 170.0 | 213.8 | 214.0 | 219.7 | 220.4 | 232.2 | 232.1 | 233.7 | 60.1 | 57.3 | 59.3 |
| 10 | 2:50:00 | 4.999 | 171.8 | 213.9 | 214.1 | 218.5 | 219.9 | 233.3 | 231.3 | 233.6 | 60.4 | 57.5 | 59.4 |
| 10 | 2:53:00 | 4.999 | 174.4 | 212.9 | 214.0 | 219.0 | 219.1 | 235.1 | 231.4 | 232.8 | 60.4 | 58.0 | 59.6 |
| 10 | 2:56:00 | 4.999 | 177.4 | 213.3 | 214.0 | 219.3 | 219.5 | 235.7 | 231.5 | 232.3 | 60.2 | 58.0 | 59.6 |
| 10 | 2:59:00 | 4.999 | 179.6 | 211.7 | 214.0 | 217.5 | 219.5 | 236.6 | 231.3 | 231.8 | 60.4 | 57.6 | 59.7 |
| 10 | 3:02:00 | 4.999 | 176.6 | 207.4 | 213.8 | 217.3 | 219.4 | 237.5 | 231.5 | 231.2 | 60.2 | 57.5 | 59.7 |
| 10 | 3:05:00 | 4.999 | 171.6 | 202.7 | 213.9 | 217.2 | 219.3 | 238.5 | 231.6 | 230.6 | 60.5 | 57.4 | 59.1 |
| 10 | 3:08:00 | 4.999 | 166.8 | 199.4 | 213.6 | 217.9 | 219.4 | 239.3 | 231.8 | 230.2 | 60.7 | 57.4 | 59.2 |
| 10 | 3:11:00 | 4.999 | 161.3 | 193.9 | 212.9 | 216.7 | 219.4 | 239.4 | 232.0 | 229.8 | 60.3 | 57.4 | 58.4 |
| 10 | 3:14:00 | 4.999 | 159.6 | 190.1 | 211.6 | 216.4 | 218.9 | 239.9 | 232.1 | 229.8 | 59.5 | 57.8 | 59.4 |

### 6.2.1 Mine-cleaned Martinka Coal Characterization

Samples of mine-cleaned Martinka coal processed in the RTU were provided by American Electric Power (AEP) at three different times: (1) coal No. 1 was received in November 1976 and was utilized for RTU shakedown operations, (2) coal Nos. 2 and 3 were received in June and July of 1977, respectively, and were utilized during the RTU operational phase of the current program. Samples of each coal were obtained for analysis from the A-3 weigh belt at frequent intervals during plant operation. All samples were analyzed at the TRW control lab for sulfate and pyritic sulfur (sulfur forms) and a portion of these were additionally analyzed by Warner Laboratories for moisture, ash, heat content, and total sulfur (short proximate analysis), as well as for sulfur forms. Warner Laboratories also performed coal iron analyses on all samples submitted.

Starting coal analyses of the mine-cleaned Martinka coals are presented in Table 6. Results from each laboratory are presented separately and then averaged for each coal. The first column of the Table lists the identifying number of the coal lot from which analytical samples were drawn. Columns two and three list the analytical laboratory and number of samples analyzed by each. Short proximate, sulfur forms, and coal iron analyses are listed in the remainder of the columns.

Analyses of coal No. 2 are presented in two parts since approximately half of coal No. 2 (Coal 2A) was stored under a partially enclosed shelter prior to processing while the other half (Coal 2B) was fully exposed to the atmospheric environment. Coal Nos. 2A and 2B were treated as distinct RTU feed coals prior to complete analysis since the extent of weathering in these two coals, and consequently their starting pyritic sulfur content, was expected to differ.

To compare coal Nos. 1, 2, and 3, consider first their respective dry short proximate analyses (ash, heat content, and total sulfur). Coal No. 1 differs significantly from coal Nos. 2A, 2B, and 3 with respect to ash content; this difference exceeds three times the largest indicated standard deviation in ash measurement. On the other hand, coals 2A, 2B, and 3 are statistically identical with respect to ash analyses. As would be expected for coals from the same mine, the same set of observations holds true with respect to coal

TABLE 6. AS RECEIVED MINE-CLEANED MARTINKA COAL ANALYSES

| Coal ID | Lab | No. of Samples | Moisture | Ash | Heat Content | $S_T$ | $S_p$ | $S_s$ | $S_o$ | Fe |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Warner | 3 | 1.32<br>±0.173 | 16.11<br>±0.261 | 12508<br>± 77 | 1.73<br>±0.045 | 0.63<br>±0.063 | 0.47<br>±0.035 | 0.63<br>±0.011 | 1.33<br>±0.010 |
|  | CTS | 14 |  |  |  |  | 0.70<br>±0.069 | 0.43<br>±0.076 |  |  |
|  | Average |  | 1.32<br>±0.173 | 16.11<br>±0.261 | 12508<br>± 77 | 1.73<br>±0.045 | 0.68<br>±0.071 | 0.43<br>±0.071 | 0.62 | 1.33<br>±0.010 |
| 2A | Warner | 8 | 0.93<br>±0.285 | 14.05<br>±0.339 | 12928<br>± 103 | 1.61<br>±0.089 | 0.62<br>±0.062 | 0.32<br>±0.058 | 0.67<br>±0.080 | 1.14<br>±0.063 |
|  | CTS | 10 |  |  |  |  | 0.79<br>±0.061 | 0.30<br>±0.041 |  |  |
|  | Average |  | 0.93<br>±0.286 | 14.05<br>±0.339 | 12928<br>± 103 | 1.61<br>±0.089 | 0.71<br>±0.107 | 0.31<br>±0.049 | 0.59 | 1.14<br>±0.063 |
| 2B | Warner | 7 | 0.79<br>±0.183 | 14.24<br>±0.354 | 12919<br>± 33 | 1.57<br>±0.059 | 0.56<br>±0.065 | 0.35<br>±0.054 | 0.66<br>±0.054 | 1.11<br>±0.059 |
|  | CTS | 16 |  |  |  |  | 0.57<br>±0.072 | 0.35<br>±0.073 |  |  |
|  | Average |  | 0.79<br>±0.183 | 14.24<br>±0.354 | 12919<br>± 33 | 1.57<br>±0.059 | 0.57<br>±0.069 | 0.35<br>±0.067 | 0.65 | 1.11<br>±0.059 |
| 2 (2A Warner plus 2B Warner & CTS) |  |  | 0.86<br>±0.170 | 14.15<br>±0.245 | 12923<br>± 54 | 1.59<br>±0.053 | 0.58<br>±0.038 | 0.34<br>±0.036 | 0.67 | 1.13<br>±0.043 |
| 3 | Warner | 10 | 1.01<br>±0.204 | 14.32<br>±0.469 | 12907<br>± 58 | 1.49<br>±0.081 | 0.60<br>±0.023 | 0.31<br>±0.029 | 0.59<br>±0.067 | 1.02<br>±0.071 |
|  | CTS | 12 |  |  |  |  | 0.67<br>±0.043 | 0.31<br>±0.026 |  |  |
|  | Average |  | 1.01<br>±0.204 | 14.32<br>±0.469 | 12907<br>± 58 | 1.49<br>±0.081 | 0.64<br>±0.051 | 0.31<br>±0.027 | 0.54 | 1.02<br>±0.071 |

heat content. Considering coal total sulfur analyses, coals 2A and 2B are statistically identical, yet differ significantly from coals 1 and 3 which differ significantly from each other. Hence, based on the short proximate analysis, coal Nos. 1. 2, and 3 differ in total sulfur while 2A and 2B are identical. These results are not surprising since the three coal samples represent output of the Martinka mine cleaning facility at three different times. Note that while the short proximate analyses of coal Nos. 1, 2, and 3 are significantly different in a statistical sense, they may not represent significant variance in output for a commercial cleaning facility.

Best estimates of the starting coal sulfur forms were generally obtained by averaging mean results from both analytical laboratories. This approach was applied to obtain sulfate sulfur estimates for all starting coals and pyritic sulfur estimates for coal Nos. 1 and 3. However, considerable bias was found between CTS and Warner analyses of $S_p$ in coal 2A; CTS and Warner analyses of 0.79 and 0.62, respectively, differ by approximately three standard deviations. Since in all other respects coal Nos. 2A and 2B appear to be identical, they should have identical $S_p$ contents. Considering that Warner analyzed coal No. 2A to have 0.62% w/w $S_p$ and that both labs agree on a 0.57% w/w $S_p$ content for coal No. 2B, the CTS analyses showing coal No. 2A to contain 0.79% w/w $S_p$ are assumed to be incorrect. Hence, the best estimate of coal No. 2 $S_p$ content was taken to be the average of available mean values, disregarding the CTS analysis of coal No. 2A. Average coal analyses thus obtained for coal Nos. 1, 2, and 3 were utilized in all ensuing leach rate evaluations.

Measured bias in sulfur forms analyses performed by CTS and Warner Laboratories is summarized graphically in Figures 15 and 16 for starting and RTU processed mine-cleaned Martinka coals. Warner analyses are plotted as a function of CTS analyses in these Figures and the zero bias line is provided for reference. Pyritic sulfur analyses are seen to be only slightly biased with most deviations from zero bias falling within the limits of combined analytical and sampling uncertainty (approximately 0.06% w/w during this experimentation as indicated by starting coal analyses). The one data grouping with bias which significantly exceeds analytical and sampling uncertainty is the previously mentioned starting analyses of coal No. 2A. Indeed, analyses

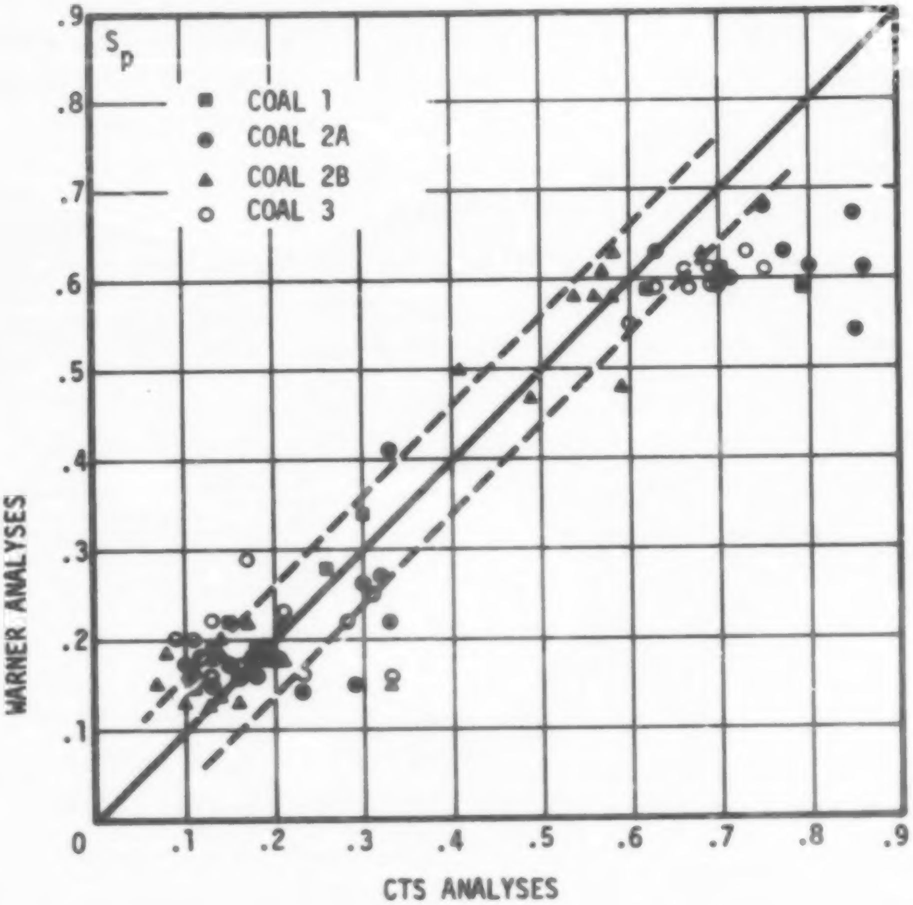


Figure 15. Comparison of Capistrano and Warner Laboratories Pyritic Sulfur Analyses

of both starting and processed coal No. 2A indicate that CTS $S_p$ analyses are biased somewhat high with respect to Warner analyses. Whether this is due to the analytical apparatus or personnel variance is not known. The generally slight bias observed is substantially smaller than the ASTM acceptable difference between two laboratories analyzing the same coal with less than 2% $S_p$, namely 0.30% w/w. Hence, obtaining best estimates of the true coal $S_p$ content by averaging results from both laboratories appears justifiable on the basis of both starting and processed coal analyses.

Bias associated with $S_s$ analyses is negligible as indicated by Figure 16. Deviations from zero bias are generally less than 0.04% w/w which corresponds

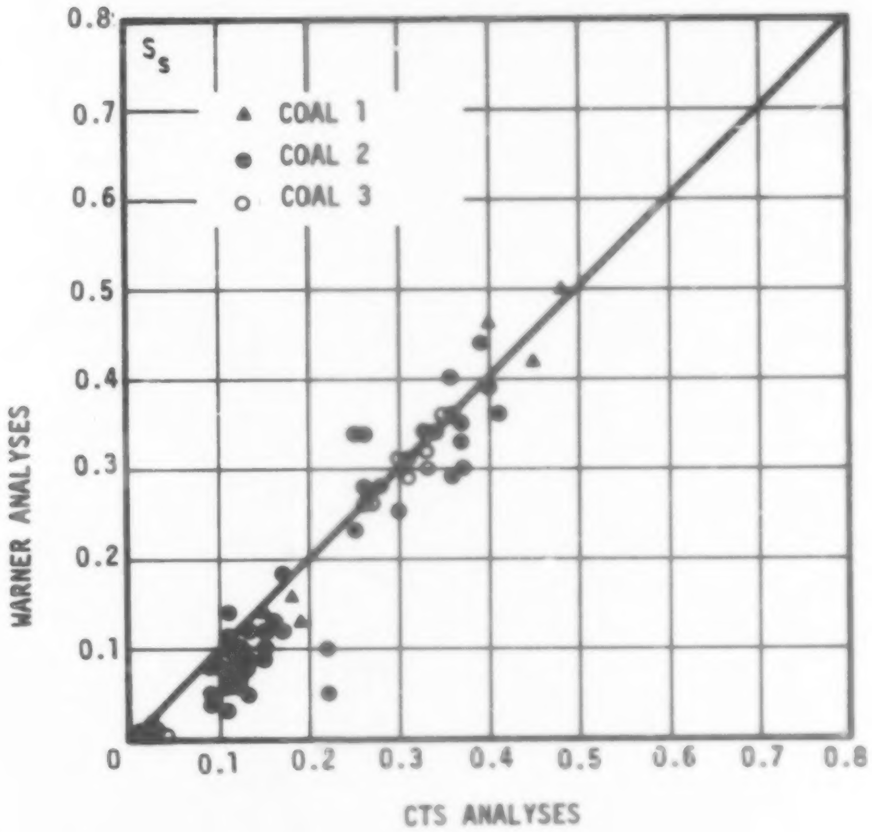


Figure 16. Comparison of Capistrano and Warner Laboratories Sulfate Sulfur Analyses

to the ASTM acceptable difference between analyses for $S_s$ by two different laboratories.

Coal samples were provided by AEP in 70 to 90 ton lots at a 1.25-inch top size. These coal samples were received by Ultrasystems, Irvine, California, where they were size reduced to approximate the nominal 14 mesh x 0 size distribution previously tested at bench scale. Size distribution data from coal Nos. 1, 2, and 3 are presented in Table 7. These data indicate good coal preparation reproducibility. A graphical comparison of these data and previously obtained bench scale size distribution data is presented in Figure 17. Coals prepared for the RTU are seen to be only slightly finer than the nominal 14 mesh x 0 mine-cleaned Martinka coal utilized during bench scale testing.

TABLE 7. SIZE DISTRIBUTION DATA FOR MINE-CLEANED MARTINKA COAL PROCESSED IN THE RTU

| Screen (Tyler Equiv.) | Opening (Microns) | Cumulative Percentages by Weight | | |
|---|---|---|---|---|
| | | Coal 1 (6 samples) | Coal 2 (8 samples) | Coal 3 (12 samples) |
| 35 | 420 | 7.9 ± 0.49 | 6.5 ± 1.14 | 8.6 ± 0.63 |
| 48 | 297 | 18.1 ± 0.68 | 14.7 ± 1.66 | 16.6 ± 0.89 |
| 100 | 149 | 43.4 ± 1.13 | 38.5 ± 2.41 | 40.9 ± 2.06 |
| 150 | 105 | 53.0 ± 1.10 | 52.0 ± 1.68 | 54.3 ± 3.20 |
| 200 | 74 | 63.5 ± 1.13 | 62.9 ± 1.42 | 68.6 ± 4.66 |

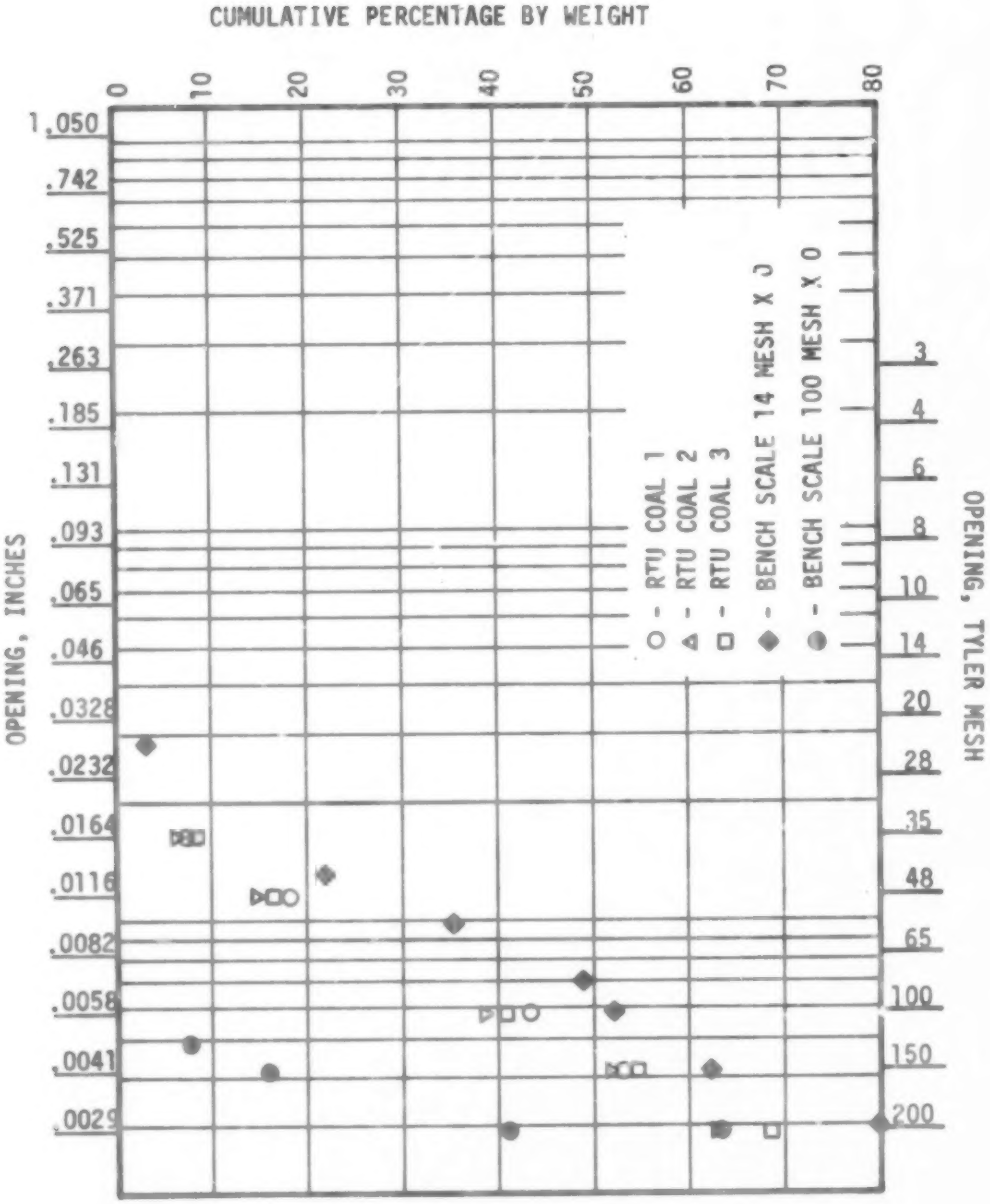


Figure 17. Mine-Cleaned Martinka Coal Size Distribution Data

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### 6.2.2 Coal Processing Data

RTU experimentation was performed under a variety of operating conditions which, at bench scale, were indicated to be suitable for demonstration of both plant operability and viability of the Meyers Process at large scale. Parameters of primary interest were varied as follows:

- Reaction temperature — $230^{\circ}F$ to $270^{\circ}F$
- Coal residence time — 5 to 10 hours
- Reagent total iron concentration — 0.0 to 4.5% w/w
- Reagent acid concentration — 0 to 4% w/w
- Oxygen partial pressure — 20 to 50 psia.

Reaction times were varied by varying the number of stages utilized in the primary reactor R-1 and/or varying the slurry feed rate. Coal feed rates of 200 to 300 pounds per hour were utilized with reagent feed rates of 1 to 2 gpm. This corresponds to a range of slurry solids concentrations from 25-33% which was tested during the RTU operational phase.

Process evaluation was based primarily on analyses of product coal samples taken from the RTU filter belt S-1. Product coal samples were generally taken from the filter belt every hour during transient plant operation and more frequently during steady state operation. Slurry samples drawn from various stages of the mixer T-2 and the reactor R-1 provided data on reagent total iron concentration, reagent Y ($Fe^{+3}$/total Fe ratio) and slurry solids.

Coal samples obtained from S-1 received a water rinse on the filter belt and were essentially free of bulk reagent. Final coal washing was performed at the CTS control lab and consisted of a slurry wash and subsequent cake wash. Slurry samples were filtered and the solids were washed; slurry filtrates were analyzed for total iron, iron forms, and sulfate content.

The water wet coal was vacuum dried at $212^{\circ}F$ for approximately 4 hours prior to toluene extraction of product elemental sulfur. The vacuum drying process was repeated after toluene extraction of the coal. Product elemental sulfur was recovered from the toluene extract by solvent distillation. Fully processed coal samples were then subjected to short proximate, sulfur forms, and iron analyses. The specific detailed procedures followed in accomplishing these operations were identical to those developed during previous bench-scale programs (4,5,11).

Bench scale testing of vacuum distillation(11) indicates that under the conditions of vacuum drying employed during the RTU program, little or no loss of elemental sulfur is incurred. Hence, vacuum drying prior to toluene extraction of processed coals was not expected to significantly affect measured product sulfate sulfur-to-elemental sulfur ratios.

Raw data from the workup and analyses of coal and reagent samples were reduced and tabulated in the desired format by computer. Computer programs written during this project to perform these computations are included in Volume II, Appendix A.

### 6.2.2.1 Pyrite Leach Rate Data--

Experimentation performed with the RTU consisted primarily of two types: 1) tests performed with acidified iron sulfate reagent and 2) tests performed with initially iron free aqueous dilute $H_2SO_4$. In the latter case, reagent iron was derived entirely from the coal being processed.

During testing with acidified iron reagent, the leach solution was recycled back to the reaction system via the leach solution storage tank T-7. This mode of operation resulted in reagent dilution from the live steam used to maintain reactor temperature since salt was not continuously added to the reagent recycle stream. Limited salt addition was employed to reduce this dilution effect. However, since reagent total iron concentration does not directly affect pyrite leach rates during simultaneous leaching-regeneration operation, reagent iron concentrations were allowed to range from 4.5% w/w to 2.7% w/w.

### Results from Processing with Acidified Iron Sulfate Reagent

Eleven sets of experimental conditions were tested (Experiment 01) with acidified iron sulfate reagent during the operational phase of the program. The initial reagent feed was composed of 4.5% w/w iron (as ferric sulfate) with 4.2% w/w $H_2SO_4$. Owing to dilution, the reagent total iron concentration ranged down to 2.7% w/w. However, a sulfate-to-iron mole ratio of approximately 2 was maintained for all tests.

A summary of the principal parameters associated with that set of experimental conditions is presented in Table 8. The experiment numbers are listed in the first column. Columns two and three list the experimental start and stop times, specified in terms of Julian day and hour. Reactor temperature, pressure and oxygen partial pressure are presented in columns four, five and six. Feed rates of coal, leach reagent and oxygen are listed in columns seven through nine. Listed in column ten are the flow rates of slurry through the R-1 circulation/oxygenation loop. Columns eleven and twelve contain the estimated mean slurry residence times in T-2 and R-1 based on the ratio of reactor volume-to-volumetric slurry flow rate. All experiments were performed utilizing only three of the available five stages of R-1, thereby maintaining relatively short residence times.

Evaluation of this experimentation was performed on the basis of $S_p$ analyses of steady state coal samples taken from the RTU filter belt. The minimum processing time required to achieve steady state operation under constant operating conditions was estimated as the ratio of utilized vessel volume (T-2 and R-1) to slurry volumetric flow rate. Verification of this steady state estimate through product coal analyses is typified by Experiment 01-03, the data from which are presented in Figure 18. Steady state for Experiment 01-03 was estimated to be attained after 7.7 hours of plant operation at the specified test conditions. Note that the product coal $S_p$ content reached a value which is constant, to within analytical precision, after only 5 hours of operation. These data are typical of all experiments performed to date with the RTU. Hence, a plug flow type steady state estimation was found to be a suitable guideline for processed coal data acquisition from the RTU.

Steady state processed coal analyses from RTU processing with iron reagent are summarized in Table 9. All steady state data are included in the presented averages. The number of processed coal samples submitted for short proximate and sulfur forms analyses are designated by xP and yF, respectively, and listed in column two of the Table. Mean R-1 reaction temperatures are listed in column three. And columns four through ten contain the average short proximate, sulfur forms and coal iron analyses. Experiments 01-04 and 01-08 are considered to be merely extensions of Experiments 01-03 and 01-07, respectively, since no effect was observed by increasing slurry recirculation rates from 20 gpm to 25 gpm. Hence, these experiments are not listed separately in Table 9.

TABLE 8. OPERATING PARAMETERS FOR ACIDIFIED IRON SULFATE REAGENT LEACH EXPERIMENTATION

| Experiment No. | Run time (day/hour) Start | Stop | R-1* Temp (°F) | R-1 Pressure (psig) | $O_2$ Pressure (psia) | Coal Feed Rate (lb/hr) | Leach Feed Rate (gpm) | $O_2$ Feed Rate (SCFH) | Recirc. Rates (gpm) | Residence time** T-2 (hrs) | R-1 (hrs) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 01-01 | 299/16:15 | 300/02:00 | 230 | 28 | 22 | 299 | 1.0 | 56 | 20 | 1.6 | 5.1 |
| 01-02 | 300/03:15 | 300/10:10 | 231 | 55 | 49 | 299 | 1.0 | 57 | 20 | 1.6 | 5.1 |
| 01-03 | 305/10:00 | 305/21:30 | 251 | 54 | 39 | 299 | 0.8 | 54 | 20 | 1.83 | 5.9 |
| 01-04 | 305/21:30 | 305/23:30 | 251 | 53 | 38 | 299 | 0.8 | 59 | 25 | 1.83 | 5.9 |
| 01-06 | 305/00:00 | 306/10:45 | 251 | 67 | 52 | 299 | 0.8 | 123 | 20 | 1.83 | 5.9 |
| 01-05 | 314/15:45 | 315/02:00 | 250 | 40-54 | 25-39 | 298 | 1.0 | 165 | 20 | 1.6 | 5.1 |
| 01-07 | 321/17:00 | 322/02:27 | 245 | 25-68 | 12-55 | 298 | 1.0 | 59 | 20 | 1.6 | 5.1 |
| 01-08 | 322/02:50 | 322/04:50 | 245 | 65 | 52 | 298 | 1.0 | 57 | 25 | 1.6 | 5.1 |
| 01-09 | 322/05:03 | 322/13:33 | 270 | 77 | 50 | 298 | 1.0 | 56 | 20 | 1.6 | 5.1 |
| 01-10 | 322/13.54 | 323/02:30 | 270 | 51 | 24 | 298 | 1.0 | 56 | 20 | 1.6 | 5.1 |
| 01-11 | 325/15:30 | 326/03:00 | 251 | 67 | 52 | 298 | 1.0 | 128 | 20 | 1.6 | 5.1 |

* The temperature of the primary reactor was varied as required for parametric investigations. T-2 mixer temperatures were the same for all experiments and ranged from approximately 170°F in the first stage to 214°F in the third stage.

** Slurry residence time is computed as the ratio of reactor volume-to-volumetric slurry flow rate.

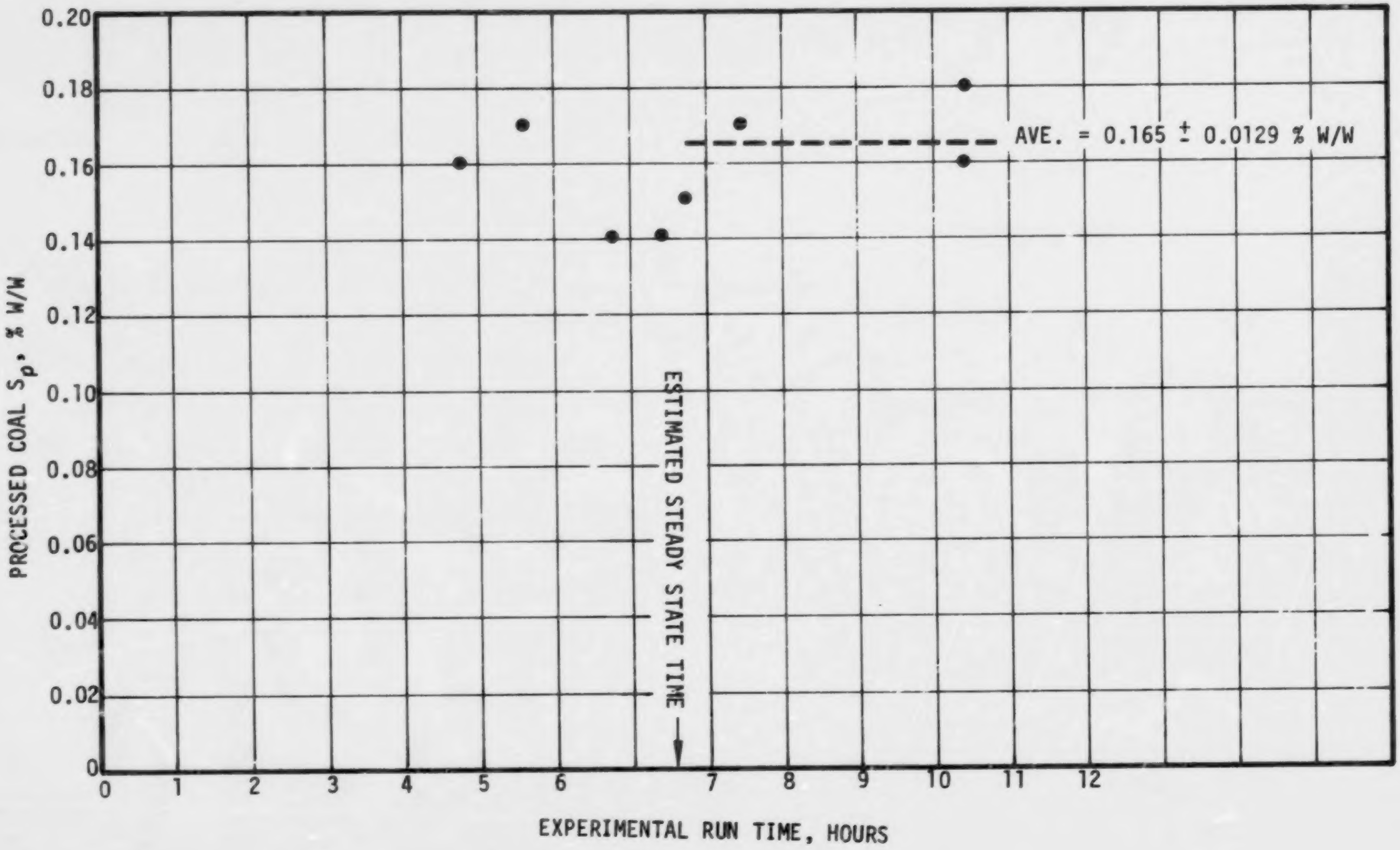

Figure 18. Pyritic Sulfur Analyses of Processed Coal from Experiment 01-03

## TABLE 9. SUMMARY OF PROCESSED COAL ANALYSES OBTAINED DURING RTU EXPERIMENTATION WITH ACIDIFIED IRON REAGENT

| Exp. No. | No. of Samples* | Processing Temp., (°F) | Coal Composition, % w/w (Except Heat Content), Dry Basis | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Ash | Heat Content, Btu/lb | Total Sulfur, $S_t$ | Pyritic Sulfur, $S_p$ | Sulfate Sulfur, $S_s$ | Organic Sulfur, $S_o$ | Iron, Fe |
| Starting Coal 2 | 15P; 31F | | 14.15<br>±0.245 | 12923<br>± 54 | 1.59<br>±0.053 | 0.58<br>±0.038 | 0.34<br>±0.036 | 0.67 | 1.13<br>±0.043 |
| 01-01 | 2P; 4F | 230 | 12.28<br>±0.212 | 13397<br>± 52 | 0.94<br>±0.000 | 0.23<br>±0.083 | 0.09<br>±0.033 | 0.62 | 0.52<br>±0.071 |
| 01-02 | 1P; 7F | 231 | 13.14 | 13300 | 0.85 | 0.25<br>±0.055 | 0.13<br>±0.120 | 0.47 | 0.46 |
| 01-03 | 3P; 6F | 251 | 12.73<br>±0.085 | 13286<br>± 65 | 1.00<br>±0.006 | 0.16<br>±0.033 | 0.09<br>±.040 | 0.75 | 0.45<br>±0.007 |
| 01-05 | 1P; 4F | 250 | 13.96 | 12888 | 0.85 | 0.16<br>±0.068 | 0.11<br>±0.025 | 0.58 | 0.53 |
| 01-06 | 2P; 4F | 251 | 12.69<br>±2.14 | 13163<br>± 299 | 0.90<br>±0.014 | 0.15<br>±0.027 | 0.11<br>±0.015 | 0.64 | 0.42<br>±0.029 |
| 01-07 | 2P; 7F | 245 | 13.32<br>±0.863 | 13123<br>± 52 | 0.87<br>±0.035 | 0.19<br>±0.075 | 0.12<br>±0.023 | 0.56 | 0.47<br>±0.021 |
| 01-09 | 1P; 3F | 270 | 10.65 | 13487 | 0.93 | 0.13<br>±0.006 | 0.18<br>±0.015 | 0.62 | 0.50 |
| 01-10 | 2P; 12F | 270 | 13.56<br>±0.636 | 13158<br>± 119 | 0.91<br>±0.092 | 0.17<br>±0.037 | 0.12<br>±0.029 | 0.62 | 0.49<br>±0.035 |
| 01-11 | 2P; 11F | 251 | 13.80<br>±0.636 | 13071<br>± 96 | 0.83<br>±0.021 | 0.16<br>±0.044 | 0.13<br>±0.025 | 0.54 | 0.55<br>±0.007 |

* The number of short proximate analyses (ash, heat content, total sulfur, and coal iron) and sulfur forms analyses (sulfate and pyritic sulfur) will be designated by xP and yF, respectively, where x and y are the number of analyses included in the indicated average. The total number of coal samples analyzed is y minus x.

Data presented in Table 9 indicate that all experiments, except for those run at the nominal 230°F temperature, resulted in product coal $S_p$ contents between 0.13% w/w and 0.19% w/w. While the 0.06% w/w spread is very nearly the limit of pyritic sulfur analytical precision, the indicated $S_p$ values are means of distinct populations obtained under different operating conditions (i.e., temperature, pressure, reagent Y) and must be treated as discrete data. Experiments 01-01 and 01-02, which were performed at nominally 230°F, resulted in product coal $S_p$ values of 0.23% w/w and 0.25% w/w, respectively.

Product coal $S_s$ contents show an average reduction of 64% corresponding to a reduction of $S_s$ from 0.34% w/w to approximately 0.12% w/w. The slightly higher product coal $S_s$ content obtained from Experiment 01-09 may be the result of combined high temperature and high oxygen partial pressure (49 psia compared to 23 psia for Experiment 01-10) since the solubilities of basic ferric sulfates, ferrous sulfate and gypsum all decrease with increasing temperature above about 212°F. However, the $S_s$ data presented in Table 9 do not generally indicate a temperature effect upon product coal sulfate contents.

The total sulfur content of the mine-cleaned Martinka coal was reduced from 1.59% w/w to 0.83-1.01% w/w under the conditions tested. Additional water washing of these product coals to reduce their $S_s$ contents to the design level of 0.02% w/w would enable products of the majority of these experiments to meet federal standards of 1.2 pounds of $SO_2$ per $10^6$ Btu.

Ash removals above those anticipated on the basis of pyrite and iron sulfate removed from ROM Martinka coals have previously been found to exceed four percent(1). However, the data presented in Table 9 shows a mean ash decrease of approximately 1.25% w/w which may be compared to the mean theoretical ash removal (based on $\Delta S_p$ and $\Delta S_s$) of 1.04% w/w. Thus, only 0.2% w/w of excess ash was removed. This is not surprising since the concentrations of reagent soluble non-pyritic mineral matter (i.e., iron oxides, iron sulfate and gypsum) are expected to be reduced by physical cleaning. That this is the case for the Martinka coals provided for this program is indicated by the fact that these coals contain little or no iron other than that associated with pyrite and iron sulfate. Although little excess ash was removed from mine cleaned Martinka coal, the removal of 1.25% w/w ash orginating from pyrite and sulfate represents an upgrading of the coal with respect to both the coal sulfur content and the coal heat value.

Correlation of these data was obtained with the previously determined pyrite leaching rate expression, namely:

$$r_L = \frac{-dW_p}{dt} = K_L W_p^2 Y^2. \qquad (1)$$

where

| | |
|---|---|
| $r_L$ | is the pyrite leaching rate, expressed in weight of pyrite removed per 100 weights of coal per hour (rate of coal pyrite conc. reduction), |
| $W_p$ | is the pyrite concentration in coal at time t in wt. percent, |
| t | is the reaction (leaching) time in hours, |
| Y | is the ferric ion-to-total iron ratio in the leacher at time t, dimensionless, and |
| $K_L$ | is the pyrite leaching rate constant (a function of temperature and coal particle size) expressed in $(\text{hours})^{-1}$ $(\text{wt. percent pyrite in coal})^{-1}$. |

with

$$K_L = A_L \exp(-E_L/RT), \qquad (2)$$

where

| | |
|---|---|
| $A_L$ | is the Arrhenius frequency factor in the units of $K_L$, |
| $E_L$ | is the apparent activation energy in calories/mole, |
| R | is the gas constant in calories/mole$^{\circ}$K, and |
| T | is the absolute temperature, in $^{\circ}$K. |

This rate expression was used in conjunction with a model of the reaction system as a series of continuous-flow stirred-tank reactors. Measured slurry temperatures and reagent Y values for each reaction stage were input for each experimental condition and the value of $K_L$ was determined at the various reaction temperatures tested.

Equation (2) indicates that a plot of ln $K_L$ vs. 1/T should yield a straight line having a slope of $-E_L/R$ and an intercept of ln $A_L$. An Arrhenius plot of the data from Experiments 01-01 through 01-11 is presented in Figure 19. A very good linear correlation was obtained. The apparent activation energy and frequency factor indicated by these data are:

$E_L$ = 26.9 Kcalories/mole, and

$A_L = 9.2 \times 10^{14}\ W_p^{-1}\ hr^{-1}$.

These values may be compared with bench scale coal processing results which yielded an $E_L$ (Bench) of 11.1 Kcalorie/mole and $A_L$ (Bench) of 2.95 x $10^5\ W_p^{-1}\ hr^{-1}$. Hence, $K_L$ (RTU) was measured to be 3 to 8 times greater than $K_L$ (Bench) for 14 mesh top-size coal at temperatures between 230°F and 270°F.

The deviations of $A_L$ and $E_L$ from the values obtained during batch reactor (bench scale) operation were only partially anticipated. The apparent value of $A_L$ was expected to increase during stagewise operation as the mixing in reaction stages deviated from ideal and the average particle residence time per stage increased. Also, under non-ideal mixing, pyrite rich particles might be expected to have longer residence times than pyrite lean particles which have a lower density. Thus, coal processing in a continuous flow stirred tank reactor is expected to result in a higher apparent $A_L$ value than would identical coal processing in a batch reactor. However, the apparent doubling of the activation energy $E_L$ above $E_L$ (bench) was not anticipated. To effect such an increase in $E_L$ requires that deviations from ideal mixing or segregation of pyrite rich coal particles increase with increasing temperature. A decrease in reagent density could increase coal segregation despite mechanical mixing and, perhaps, selectively cause the pyrite rich coal particles to remain longer in each reaction stage. While density changes due to temperature alone are small, this effect coupled with reagent dilution can be significant. Note that the conditions of Experiment 01 were performed in the order of increasing temperature (Table 8) and that, as previously stated, the reagent total iron was reduced from 4.5% w/w to 2.7% w/w by dilution with process steam. The combined temperature and dilution effects are estimated to have resulted in mean reagent densities of 1.15 gm/cc during 230°F tests, 1.08 gm/cc during 250°F tests and 1.06 gm/cc during 270°F tests. Thus, significant reagent density differences occurred between the 230°F and 270°F

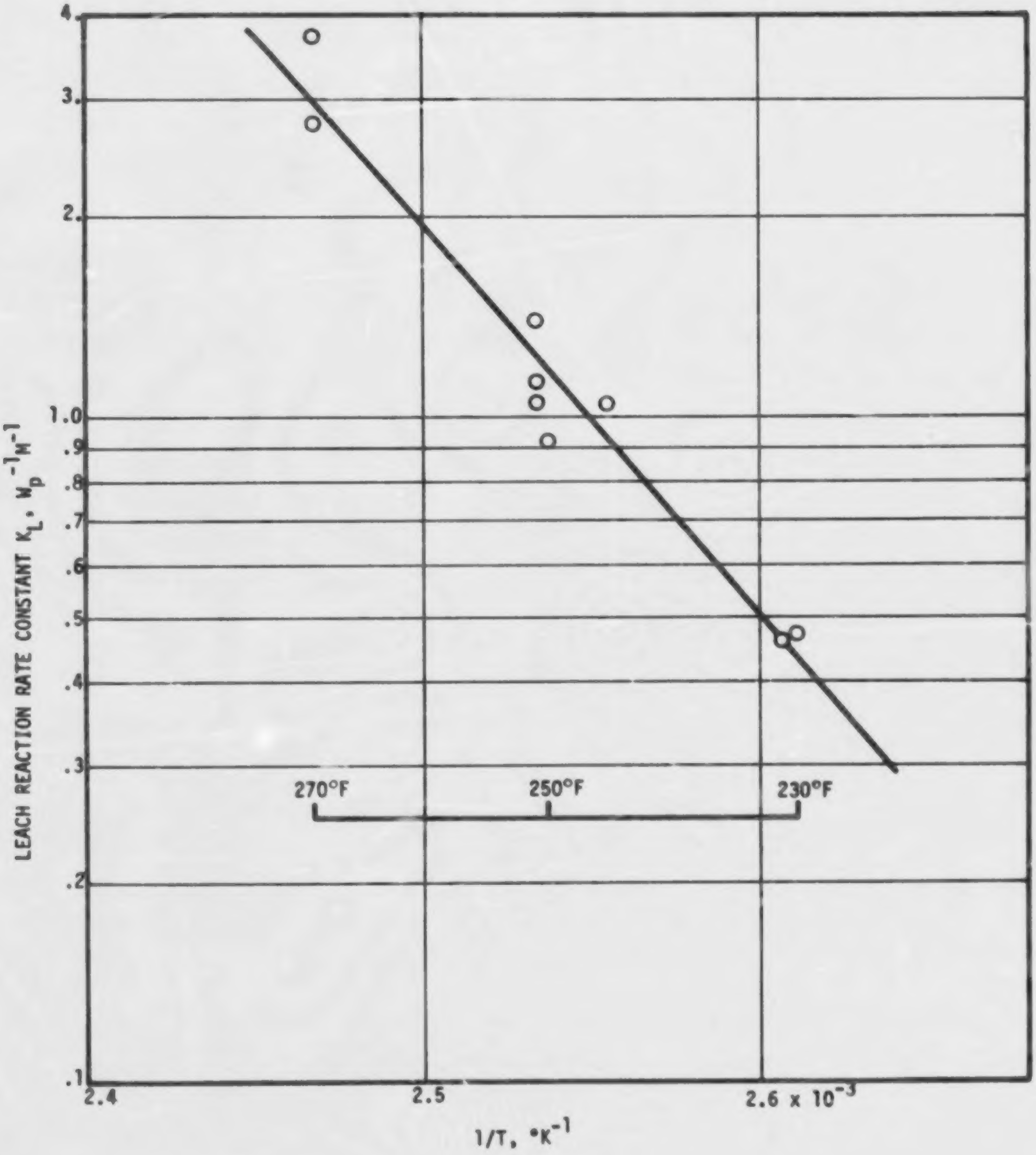

Figure 19. Arrhenius Plot of Data from RTU Experiments 01-01 to 01-11

experimentation which may have resulted in the apparent increase in the pyrite leaching activation energy. Whether or not this density difference is in itself sufficient to cause the observed factor of 2 increase in activation energy cannot be determined from available data. However, if the observed increase is the result of a density effect then reagent density would become an important reaction design parameter for systems utilizing stirred tank reactors.

## Results from RTU Processing with Low Iron Reagent

Two groups of experiments were performed in the RTU with low iron reagent: (1) shakedown experimentation with coal 1 using pure water feed reagent and (2) processing of coal 3 with acidified reagent during the RTU operational phase (Experiment 03). Both groups of experiments were performed utilizing all five stages of R-1 rather than the three stages used in Experiment 01. Thus, longer reaction times were obtained for similar slurry feed rates.

Operating parameters for low iron reagent experimentation are listed in Table 10. Shakedown experiments 8 and 9 were performed with pure water feed and coal derived iron and sulfate. Experiment 03 was performed with a nominal 1% w/w $H_2SO_4$ feed solution. However, due to inadequate reagent mixing in tank T-8, acid segregation in the reagent solution resulted in a 2% w/w acid feed reagent for experimental condition 03-03. The difference between 1% and 2% starting reagent acid concentration is not significant since acid addition serves only to prevent iron oxide deposition from the reagent and possible subsequent sulfate occlusion on the coal or blinding of the pyrite surfaces. The pH of these solutions ranges from 1.0 to 1.2 and either pH is sufficiently low to suppress precipitation of iron oxide from the reagent.

A summary of processed coal analyses from low iron reagent processing is presented in Table 11. Replicate shakedown experiments 8 and 9 show an $S_p$ reduction of 57% from 0.68% w/w to approximately 0.27% w/w during 265°F processing. The sulfur forms analyses problem observed during Experiment 8 (i.e., the high $S_o$ and low $S_p$) is most likely attributable to inefficient pyrite extraction; the expected $S_o$ based on ash removal is 0.63% w/w which would indicate a true $S_p$ value of 0.26% w/w. Experimentation performed with acidified reagent at 230°F indicates $S_p$ removals from 0.64% w/w to approximately 0.16% w/w or 75%.

## TABLE 10. OPERATING PARAMETERS FOR LOW IRON REAGENT LEACH EXPERIMENTATION

| Experiment No. | Run time (day/hour) Start | Run time (day/hour) Stop | Reagent $H_2SO_4$ Concentration (% w/w) | R-1 Temp (°F) | R-1 Pressure (psig) | $O_2$ Pressure (psia) | Coal Feed Rate (lb/hr) | Reagent Feed Rate (gpm) | $O_2$ Feed Rate (SCFH) | Recirc. Rates (gpm) | Residence time* T-2 (hrs) | Residence time* R-1 (hrs) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 (Shakedown) | 238/12:00 | 238/22:41 | 0 | 265 | 50 | 26 | 198 | 1.0 | 94 | 23** | 1.9 | 9.5 |
| 9 (Shakedown) | 249/11:15 | 249/22:31 | 0 | 265 | 50 | 26 | 198 | 1.0 | 103 | 16** | 1.9 | 9.5 |
| 03-01 | 6/17:04 | 7/03:00 | 1 | 222 | 31 | 28 | 198 | 1.7 | 94 | 20 | 1.1 | 5.7 |
| 03-02 | 9/12:00 | 10/03:20 | 1 | 232 | 41 | 34 | 199 | 1.2 | 88 | 20 | 1.6 | 8.2 |
| 03-03 | 10/17:07 | 11/07:28 | 2 | 234 | 41 | 33 | 199 | 1.2 | 150 | 20 | 1.6 | 8.2 |

* Slurry residence time is computed as the ratio of reactor volume-to-volumetric slurry flow rate.

** Recirculation piping used during shakedown processing was 1.25 inch sch. 80 pipe while that used during Phase III processing was 0.75 inch sch. 40 pipe.

## TABLE 11. SUMMARY OF PROCESSED COAL ANALYSES OBTAINED DURING RTU EXPERIMENTATION WITH LOW IRON REAGENT

| Exp. No. | No. of Samples* | Processing Temp., (°F) | Coal Composition, % w/w (Except Heat Content), Dry Basis | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Ash | Heat Content, Btu/lb | Total Sulfur, $S_t$ | Pyritic Sulfur, $S_p$ | Sulfate Sulfur, $S_s$ | Organic Sulfur, $S_o$ | Iron, Fe |
| Starting Coal 1 | 3P; 14F | | 16.11<br>±0.261 | 12508<br>± 77 | 1.73<br>±0.045 | 0.68<br>±0.071 | 0.43<br>±0.071 | 0.62 | 1.33<br>±0.010 |
| 8 (Shakedown) | 1P; 5F | 265 | 13.83 | 12985 | 1.03 | 0.17?<br>±0.061 | 0.14<br>±0.025 | 0.72? | 0.88 |
| 9 (Shakedown) | 1P; 5F | 265 | 12.33 | 13213 | 1.07 | 0.29<br>±0.021 | 0.15<br>±0.007 | 0.63 | 0.71 |
| Starting Coal 3 | 10P; 22F | | 14.32<br>±0.469 | 12907<br>± 58 | 1.49<br>±0.081 | 0.64<br>±0.051 | 0.31<br>±0.027 | 0.54 | 1.02<br>±0.071 |
| 03-01** | 4P; 8F | 222 | 12.97<br>±0.894 | 13258<br>± 162 | 0.68<br>±0.044 | 0.18<br>±0.064 | 0.01<br>±0.010 | 0.49 | 0.23<br>±0.029 |
| 03-02** | 4P; 11F | 232 | 12.02<br>±0.636 | 13388<br>± 91 | 0.78<br>±0.065 | 0.17<br>±0.042 | 0.01<br>±0.006 | 0.60 | 0.26<br>±0.049 |
| 03-03** | 4P; 9F | 234 | 12.51<br>±0.953 | 13265<br>± 155 | 0.75<br>±0.033 | 0.14<br>±0.031 | 0.02<br>±0.007 | 0.59 | 0.25<br>±0.060 |

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* The number of short proximate analyses (ash, heat content, total sulfur and coal iron) and sulfur forms analyses (sulfate and pyritic sulfur) will be designated by xP and yF, respectively, where x and y are the number of analyses included in the indicated average. The number of coal samples analyzed is y minus x.

** These experiments were performed with 1 to 2% w/w $H_2SO_4$ reagent.

These results are somewhat surprising since higher $S_p$ removals are expected at higher processing temperatures for coals from the same mine having nearly identical starting $S_p$ contents and processed under similar oxygen partial pressures and throughputs. The observed difference could be due to several things, including: (1) differences between the pyrite particle sizes and distributions in coal Nos. 1 and 3; (2) differences in oxygen availability and (3) the effect of reagent acidification. That coal Nos. 1 and 3 differ with respect to pyrite particle size and distribution appears feasible since they are known to differ in other respects (i.e., ash and organic sulfur contents). The higher ash coal No. 1 may contain pyrite which is difficult to remove owing to its low specific surface area. Oxygen availability is important to pyrite leach rates obtained during low iron reagent processing. Because the bulk reagent contains very little iron, continuous and efficient regeneration of reagent ferric ion is necessary to maintain high pyrite leach rates. The recirculation/oxygenation loop used during shakedown was 1.25-inch schedule 80 pipe while that used during Phase III operation was 0.75-inch schedule 40 pipe. Thus, flow velocities in the regenerator during shakedown were approximately 40% of those obtained during Phase III operation (the associated shakedown Reynolds number was approximately 66% of that in Phase III). Since gas-reagent mixing efficiency, and therefore oxygenation, may relate to recirculation flow velocities, slurry oxygenation obtained during shakedown experimentation may have been less efficient than that obtained during Phase III operation.

Thus, the specific cause of differences in pyrite leach rates obtained during low iron processing of coal Nos. 1 and 3 cannot be accurately defined on the basis of available data. Further experimentation, including leaching of coal Nos. 1 and 3 with high iron reagent, would be required before confident conclusions can be drawn.

Differences in product coal $S_s$ contents indicated in Table 11 are due to the fact that samples from Experiments 8 and 9 were not washed in the laboratory prior to analysis. However, bench scale experimentation performed to date with acidified and non-acidified water reagents has not indicated an appreciable difference in processed coal $S_s$ contents. It, therefore, appears that further washing would effect essentially complete sulfate removal from

Experiments 8 and 9 as was the case for Experiments 03-01 to 03-03. Note that all processed coals from Experiment 03-03 contain less than 1.2 pounds $SO_2$ per $10^6$ Btu.

Data from low iron reagent processing may be compared with 4% iron reagent processing data obtained at similar temperatures and $O_2$ partial pressures. Experiments 01-10 and 01-01 were performed at $270^0F$ and $230^0F$, respectively, with $O_2$ pressures of approximately 23 psia. A residence time of 5.1 hours at elevated temperature and pressure was used for both Experiment 01 conditions. A comparison of data from Experiment 01-10 (Table 9) and Experiments 8 and 9 indicates that similar $\Delta S_p$ values were obtained from both groups of experiments although only half as much residence time was required with iron reagent. Thus, higher pyrite leach rates were obtained during processing with iron reagent. On the other hand, extrapolation of the results from Experiment 01-01 (residence time of 5.1 hours) to the 5.7 and 8.2 hours of residence time utilized in Experiments 03-01 through 03-03 yields essentially the same results which were obtained in Experiment 03. That is, assuming that the effective pore reagent Y value for low iron reagent processing experiments was similar to that of Experiment 01-01, processed coal analyses from Experiment 03 appear to indicate pyrite leach rates similar to those obtained during the higher iron reagent Experiment 01-01.

As mentioned previously, Coal No. 1 reacted at a lower rate than did Coal No. 3 under low iron reagent processing conditions. The comparison of Experiments 8 and 9 with Experiment 01-10 indicates that Coal No. 1 also reacted slower than did Coal No. 2 which was processed with a higher iron content reagent. The comparison of Experiment 03 with Experiment 01-01 indicates that Coal No. 3 processed with acidified low iron reagent reacted at a rate comparable to that obtained from higher iron reagent processing of Coal No. 2. The conclusion drawn from these observations depends on the assumed reaction rate of Coal No. 2 relative to Coal Nos. 1 and 3. Since all three coals are products of the same mine and physical cleaning facility and were processed at the same top-size, it seems reasonable to expect that these coals would react at similar rates under similar processing conditions. If this expectation is correct then the lower rates obtained during Experiments 8 and 9 are most probably due to inefficient oxygenation. Further, Experiments 01-01 and 03 indicate that reaction rates measured in the RTU were not affected by reagent total iron content up to a concentration of 4.5% w/w.

Coal processed in the RTU with acidified low iron reagent was found to contain approximately 0.1% w/w less $S_s$ after the control lab washing stages than did coals processed with 4% iron reagent. This observation is not considered to be reflective of differences in process chemistry but, rather, indicates the necessity of effective pore solution displacement during the washing of coals processed with high iron reagent.

### 6.2.2.2 Reagent Regeneration Data--

Each stage of the R-1 reactor is provided with a slurry recirculation/oxygenation loop which promotes reagent regeneration concurrently with pyrite leaching. During RTU operation the oxygen feed was proportionated among the reaction stages according to estimated regeneration requirements occurring at each stage. An excess of oxygen was fed to each stage of the RTU which corresponded to between 4 and 7 times the actual stoichiometric requirement.

Bench scale experimentation has shown that under such operation, the reagent regeneration rate may be expressed as follows:

$$r_R = -\frac{dFe^{+2}}{dt} = K_R\, P_{O_2}\, (Fe^{+2})^2, \qquad (3)$$

where

| | |
|---|---|
| $r_R$ | is the moles of ferric ion regenerated per unit time, |
| $P_{O_2}$ | is the partial pressure of oxygen in atmospheres, |
| $Fe^{+2}$ | is the ferrous ion concentration in moles per liter, |
| $K_R$ | is the rate constant, a function of temperature only, in liters/mole-atm-unit time, |

and

$$K_R = A_R \exp(-E_R/RT) \qquad (4)$$

with

$A_R = 6.7 \times 10^5$ liters/mole-atm-min., and

$E_R = 13.2$ Kcal/mole.

The bench scale determined $E_R$ value should apply to RTU regeneration since reagent, unlike coal particles, is not prone to segregation and ideal flow through the staged reactor system should be closely approximated. On the other hand, values of $A_R$ computed from RTU data may differ from that determined at bench scale since the extent or efficiency of regeneration may be different. Hence, the $E_R$ value of 13.2 Kcal/mole was assumed to be correct for RTU processing and the value of $A_R$ (RTU) was computed from process data.

Computation of reagent regeneration rates in R-1 requires data on inlet and outlet reagent total iron concentrations and Y values, steady state Y data for each reactor stage, $O_2$ pressure data, and $Fe^{+2}$ generation rates. Of these required data, only the $Fe^{+2}$ generation rates are not directly measured during processing. The major source of $Fe^{+2}$ generation is the pyrite leach reaction which was discussed in Section 6.2.2.1. A secondary source of $Fe^{+2}$ is reaction between ferric ion and the coal matrix. Although the extent of this oxidation reaction is too small to be detected by heat content analysis of the coal, sufficient $Fe^{+2}$ is produced to warrant accounting during regeneration rate computation. The quantity of $Fe^{+2}$ generated above that expected from pyrite leaching is termed excess $Fe^{+2}$.

Bench scale data from processing 14 mesh x 0 mine cleaned Martinka coal with 5% w/w iron reagent at 212°F are presented in Table 12 (Reference 8). These data indicate an excess $Fe^{+2}$ generation rate of approximately 0.005 weights of $Fe^{+2}$ per weight of coal per hour during the first 5 hours of processing. Subsequent processing resulted in little or no additional excess $Fe^{+2}$ generation. These data provided the basis for estimating the rate of excess $Fe^{+2}$ generation during RTU coal processing.

Equations (1) through (4) were used with steady state data from Experiment 01 to determine regeneration efficiency in the RTU. Since attainment of steady state with respect to reagent Y required long processing times for conditions of Experiment 01, not all conditions of this experiment provided true steady state reagent Y data. Conditions 02, 03, 06, and 10 all provided steady state or near steady state Y data while conditions 01, 05, 07, 09, and 11 yielded only transient data. Experiments 01-04 and 01-08 were short term tests involving pulse response.measurements only in the second stage of reaction and cannot be used for overall regeneration rate evaluation.

TABLE 12. EXCESS $Fe^{+2}$ GENERATION DATA FROM PROCESSING 14 MESH x 0 MINE CLEANED MARTINKA COAL WITH 5% w/w IRON REAGENT

| | | | Excess $Fe^{+2}$ Generation | |
|---|---|---|---|---|
| Exp. No. | Temp. ($^oF$) | Process Time (hrs) | $\frac{\text{weight } Fe^{+2}}{\text{weight coal}}$ | $\frac{\text{weight } Fe^{+2}}{\text{weight coal-hr}}$ |
| B.S. 35 | 212 | 5 | 0.0258 | 0.0052 |
| B.S. 27 | 212 | 24 | 0.0197 | 0.0008 |
| B.S. 28 | 212 | 48 | 0.0294 | 0.0006 |

It should be noted that rapid attainment of steady state processed coal $S_p$ contents relative to times required to obtain steady state reagent Y values is indicative of the fact that product coal analyses are rather insensitive to small changes in reagent Y. This is particularly true when coal $S_p$ contents are reduced to 0.20% w/w or less.

Examples of transient and near steady state reagent Y data are illustrated in Figure 20. Reagent Y data from Experiments 01-01 and 01-02 are presented in the Figure as a function of process time. Data from Experiment 01-01 indicate that the reagent Y is decreasing with time at a substantial rate in all stages. Increasing the partial pressure of oxygen from 22 psia to 49 psia (Experiment 01-02) is seen to have essentially stabilized the reagent Y value in each stage. Although data from Experiment 01-02 indicate that the first and second stage Y values may have still been changing at the test conclusion, the rate of change appears to be rather small. Note that the stage two Y value should not exceed that of stage three and that the first stage Y value should not exceed that of stage two since $Fe^{+2}$ generation due to $S_p$ removal decreases with each successive stage. Thus, the true steady state Y values of the first two stages probably do not differ from the measured values by more than about 0.02 which will not substantially affect regeneration rate estimation.

Regeneration rate estimates computed from Experiments 01-02, 01-03, 01-06, and 01-10 are presented in Table 13. Reaction temperature, oxygen partial pressure and oxygen feed rate data are listed in columns two, three, and four.

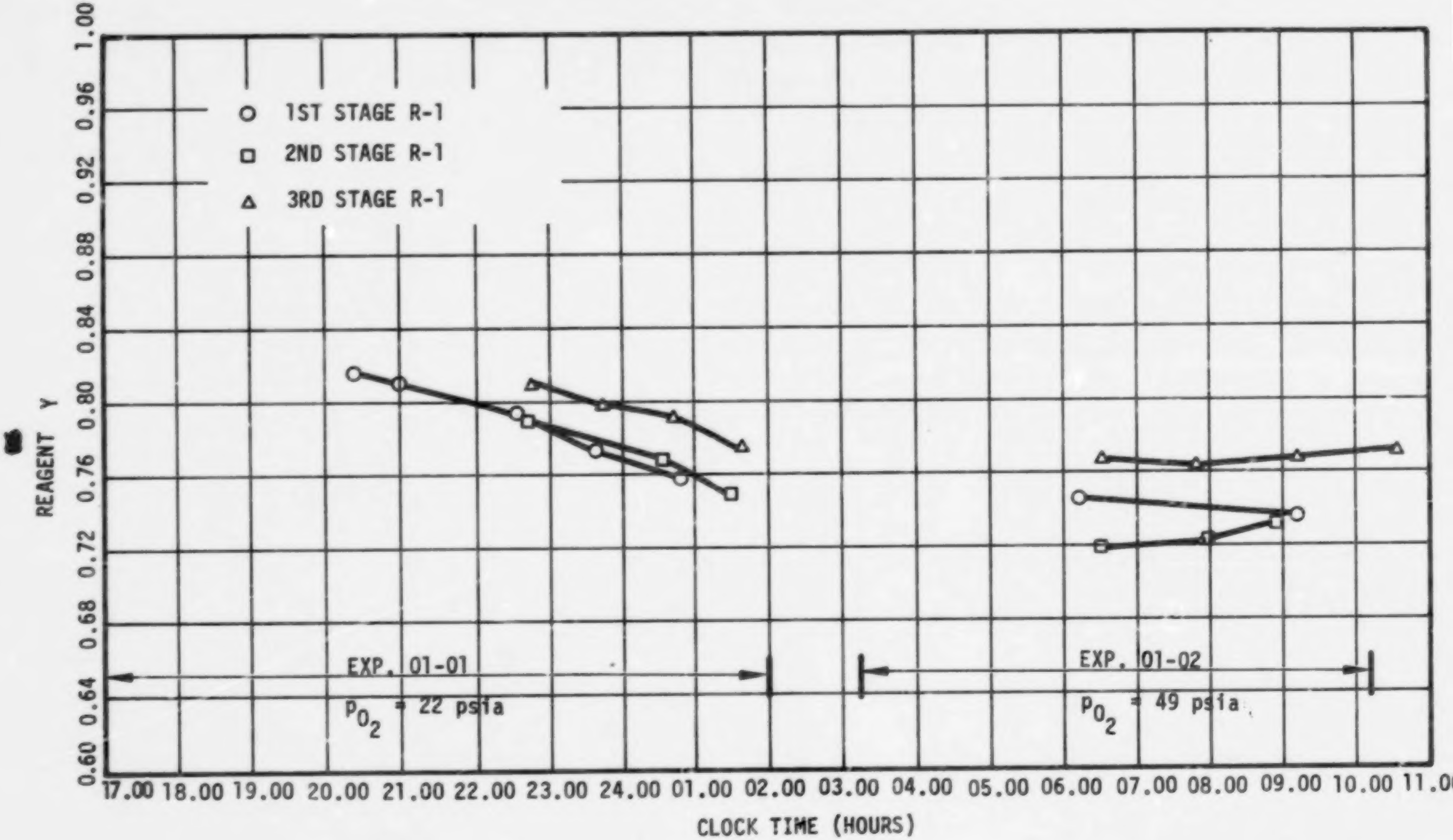

Figure 20. Reagent Y Data From RTU Processing Experiments 01-01 And 01-02

## TABLE 13. RTU REAGENT REGENERATION DATA

| Exp. No. | Temp. (°F) | $P_{O_2}$ (psia) | $O_2$ Feed Rate (SCFH) | XS $Fe^2$ Generation $\left(\frac{\text{wt. } Fe^2}{\text{wt. coal-hr}}\right)$ | $A_R x10^{-5}$ $\left(\frac{\text{liter}}{\text{mole-atm-min}}\right)$ | | | | % of Bench Scale $A_R$ | Average $K_R x10^3$ $\left(\frac{\text{liter}}{\text{mole-atm-min}}\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Stage 1 | Stage 2 | Stage 3 | Average | | |
| 01-02 | 231 | 49 | 57 | 0.0 | 1.33 | 1.16 | 0.78 | 1.09 | 16 | 3.28 |
| | | | | 0.005 (bench scale) | 2.70 | 2.51 | 2.09 | 2.43 | 36 | 7.32 |
| | | | | 0.010 | 4.08 | 3.85 | 3.70 | 3.88 | 57 | 11.68 |
| 01-03 | 251 | 39 | 54 | 0.0 | 0.72 | 0.66 | 1.10 | 0.83 | 12 | 4.07 |
| | | | | 0.005 (bench scale) | 1.50 | 1.44 | 2.18 | 1.71 | 25 | 8.39 |
| | | | | 0.010 | 2.29 | 2.21 | 3.25 | 2.58 | 39 | 12.65 |
| 01-06 | 251 | 52 | 123 | 0.0 | 0.58 | 0.79 | 1.04 | 0.80 | 12 | 3.92 |
| | | | | 0.005 (bench scale) | 1.16 | 1.47 | 2.06 | 1.56 | 23 | 7.65 |
| | | | | 0.010 | 1.72 | 2.14 | 3.07 | 2.31 | 35 | 11.33 |
| 01-10 | 270 | 23 | 56 | 0.0 | 0.01 | 0.41 | 0.29 | 0.24 | 4 | 1.82 |
| | | | | 0.005 (bench scale) | 0.60 | 0.95 | 0.81 | 0.79 | 12 | 6.01 |
| | | | | 0.010 | 1.18 | 1.47 | 1.33 | 1.33 | 20 | 10.11 |
| | | | | 0.020 | 2.34 | 2.52 | 2.35 | 2.40 | 36 | 18.24 |

The value of $A_R$ was estimated for each reaction stage based on an excess $Fe^{+2}$ generation rate of from zero to four times the value measured at bench scale, and an $E_R$ value of 13.2 Kcal/mole; the assumed excess $Fe^{+2}$ generation and corresponding $A_R$ values are listed in columns five through nine. The average $A_R$ values obtained in the RTU are listed in column ten as a percentage of the bench scale $A_R$ value. The average measured $K_R$ values from this testing are listed for reference in the last column.

Rate constant data presented in Table 13 for a fixed level of excess $Fe^{+2}$ generation indicate little temperature dependence (Experiments 01-02, 01-03, and 01-06) or show a rate decrease with increasing temperature (Experiments 01-02, 01-03, and 01-06 compared to Experiment 01-10). Since the temperature effect on reagent regeneration is known with confidence, these data must indicate that excess $Fe^{+2}$ generation is not a constant, but rather a function of temperature which increases with increasing temperature. As such, higher excess $Fe^{+2}$ generation rates and, therefore, higher $K_R$ values apply for higher processing temperatures. If the bench scale excess $Fe^{+2}$ generation rate is assumed to be correct up to 230°F, then the excess rate must double with each additional 20°F increment for the data to support an $E_R$ value of 13.2 Kcal/mole. Twice the bench scale excess must apply at 250°F and four times the bench scale excess must apply at 270°F. This observation is in agreement with bench scale data indicating that excess ferric ion consumption increases by at least a factor of two between 212°F and 250°F when processing 14 mesh x 0 mine cleaned Martinka coal(11). Thus, these data appear to indicate that regeneration in the RTU proceeded with an $A_R$ (RTU) of approximately $2.4 \times 10^5$ liters/mole-atm-min or at 37% of the rate obtained at bench scale. This represents an estimate of the minimum average regeneration rate obtained in the RTU since excess $Fe^{+2}$ generation rates at 230°F may actually be higher than those measured at 212°F.

These data also indicate that increasing the oxygen throughput from a four-fold to a fourteen-fold stoichiometric excess did not improve regeneration rates (compare Experiments 01-03 and 01-06).

If indeed the regeneration efficiency in the RTU is 37% with respect to bench scale regeneration, then a comparison of the two regeneration systems is appropriate. The primary parameters of concern are the oxygen-reagent blending path length, Reynolds number and gas-reagent contact frequency (stage turnaround time through the regenerator loop). These parameters compare as follows:

- Both the RTU and bench scale systems have gas-slurry mixing path lengths on the order of 10 feet. Both systems also have bends up to about $90^0$ at some point. The bench unit, however, has a valved constriction in the mixing path which may double the fluid velocity at the valve. The RTU unit contains no flow constrictions.
- The RTU system circulates slurry at a rate of 20 gpm through 0.82-inch I.D. pipe while the bench unit circulates slurry at a rate of 1 gpm through a 0.75-inch I.D. tube. A ratio of the Reynolds numbers obtained in the RTU and bench unit mixing regions may be computed to avoid estimating viscosities of slurries at the reaction temperature. The ratio Re(RTU)/Re(Bench) based on an estimated 50% constriction in the bench scale tubing is approximately nine.
- Each stage of the RTU contained approximately 150 gallons of slurry which was circulated through the regeneration loop at a rate of 20 gpm giving a slurry turnaround time of approximately 7.5 minutes. The bench scale reactor generally contained about 1.6 gallons which was circulated at 1 gpm for a turnaround time of approximately 1.5 minutes.

From these facts, it appears that oxygen-slurry mixing was at least as vigorous in the RTU system as it was in the bench scale apparatus. Any additional gas-slurry blending due to the restriction in the bench circulation line should be compensated for, at least in part, by the higher overall Reynolds number obtained in the RTU circulation lines. Hence, the principal difference between the two systems resides in their respective stage turnaround times through slurry circulation/oxygenation loops; bench scale reactor turnaround times through the oxygenation loop were only one-fifth as long as RTU turnaround times.

That the regeneration efficiency should relate to slurry turnaround time through the regeneration loop appears reasonable if the oxygen bubbles coalesce and disentrain from the slurry at a reasonably rapid rate (on the order of minutes) after slurry reentry into the reactor. The regeneration rate expression (Equation 3) is expressed in terms of oxygen partial pressure but, more fundamentally, the regeneration rate is proportional to the concentration of dissolved oxygen. The concentration of dissolved oxygen depends on the rate of pyrite leaching and the rate of oxygen dissolution into the reagent. The latter depends on the partial pressure of oxygen and the gas-reagent contact area. Since, under conditions of rapid oxygen disentrainment the gas-reagent contact area outside the circulation loop decreases rapidly with time, regeneration efficiency would be expected to increase with decreasing stage turnaround time through the recirculation loop. Assuming that this hypothesis is correct, it would appear that to increase regeneration rates in the RTU would require an increase in the slurry recirculation rate (though not necessarily the Reynolds number) and/or the partial pressure of oxygen.

### 6.2.2.3 Elemental Sulfur Recovery--

All coal samples drawn from the RTU were extracted with toluene to recover product elemental sulfur ($S_n$) prior to sulfur forms analyses. The quantity of $S_n$ generated during processing is determined by analyses of toluene extracts from filter belt coal samples. Additionally, $S_n$ recovery has been determined for a limited number of samples from the primary reactor.

Results of $S_n$ extractions performed during RTU shakedown and Experiments 01 and 03 are presented in Table 14. Included in this table are the quantity of residue composed of sulfur and tar, sulfur content of the residue (based on one analysis per sample) and $S_n$ content of the coal based on extraction data. Results from double toluene extractions are indicated by two tar and sulfur content values. Sample coal analysis data used in computation of the product ratio $S_s/S_n$ are also presented. The last column of the table lists the product sulfur ratio $S_s/S_n$ which is estimated as $(\Delta S_p - S_n)/S_n$. These data were obtained identically for all experimentation with the exception that twice as much toluene extract was distilled to generate the sulfur-tar residue for Experiment 03 than was used for the preceding experimentation. Also, balance precision was increased from 0.005 gram to 0.00005 gram for Experiment 03. The resultant improved precision is evidenced by the relative $S_s/S_n$ data scatter obtained before and after initiation of Experiment 03, namely ±1.66 compared to ±0.71. Thus, the substantial scatter in $S_s/S_n$ data obtained prior to Experiment 03 is principally due to extraction residue weighing inaccuracies. That these inaccuracies were essentially random is verified by the fact that the mean $S_s/S_n$ ratio from combined shakedown and Experiment 01 testing and from

TABLE 14. ELEMENTAL SULFUR PRODUCT GENERATION DATA FROM RTU PROCESSING

| Experiment # | Sample ID | Sulfur + Tar Residue (% w/w) | Sulfur Content (%) | Elemental Sulfur, $S_n$ (% w/w) | Coal Analysis, % w/w | | | $S_s/S_n$ * |
|---|---|---|---|---|---|---|---|---|
| | | | | | $S_p^o$ | $S_p^f$ | $\Delta S_p$ | |
| 8 (Shakedown) | S1 1900 | 0.67 | 11.31 | 0.08 | 0.68 | 0.21 | 0.47 | 5.18 |
| | S1 2000 | 0.92 | 13.28 | 0.12 | 0.68 | 0.17 | 0.51 | 3.19 |
| | S1 2200 | 0.76 | 25.62 | 0.19 | 0.68 | 0.07 | 0.61 | 2.12 |
| 9 (Shakedown) | S1 1800 | 0.76 | 12.61 | 0.10 | 0.68 | 0.32 | 0.36 | 2.60 |
| | S1 2000 | 0.88 | 12.95 | 0.11 | 0.68 | 0.32 | 0.36 | 2.27 |
| | S1 2101 | 0.97 | 9.11 | 0.09 | 0.68 | 0.23 | 0.44 | 4.00 |
| | S1 2331 | 0.73 | 22.33 | 0.16 | 0.68 | 0.33 | 0.35 | 1.15 |
| 01-01 | M7 0130 | 0.41 | 26.2 | 0.11 | 0.58 | 0.24 | 0.34 | 2.09 |
| | M7 2105 | 0.32 | 44.8 | 0.14 | 0.58 | 0.21 | 0.37 | 1.64 |
| | S1 2345 | 0.52 | 39.2 | 0.20 | 0.58 | 0.23 | 0.35 | 0.75 |
| | S1 0157 | 0.31 | 41.1 | 0.13 | 0.58 | 0.29 | 0.29 | 1.23 |
| 01-02 | S1 0745 | 0.55 | 54.8 | 0.30 | 0.58 | 0.33 | 0.25 | 0 |
| | S1 0942 | 0.55 | 56.8 | 0.31 | 0.58 | 0.22 | 0.36 | 0.13 |
| 01-03 | M7 2103 | 0.78 | 42.6 | 0.33 | 0.58 | 0.30 | 0.28 | 0 |
| | S1 2125 | 0.65 | 11.9 | 0.08 | 0.58 | 0.17 | 0.41 | 4.13 |
| 01-05 | M7 1940 | 0.75 | 57.7 | 0.43 | 0.58 | 0.13 | 0.45 | 0.05 |
| | S1 1910 | 0.45 | 44.7 | 0.20 | 0.58 | 0.17 | 0.36 | 0.80 |
| | S1 1950 | 0.52 | 48.8 | 0.25 | 0.58 | 0.16 | 0.37 | 0.48 |
| 01-06 | S1 1050 | 0.32 | 50.9 | 0.16 | 0.58 | 0.13 | 0.45 | 1.81 |
| 01-07 | S1 0144 | 0.17 | 31.1 | 0.05 | 0.58 | 0.20 | 0.38 | 6.60 |
| | S1 0235 | 0.15 | 48.6 | 0.07 | 0.58 | 0.33 | 0.25 | 2.57 |

- Continued -

TABLE 14. (Continued)

| Experiment # | Sample ID | Sulfur + Tar Residue (% w/w) | Sulfur Content (%) | Elemental Sulfur, $S_n$ (% w/w) | Coal Analysis, % w/w | | | $S_s/S_n$* |
|---|---|---|---|---|---|---|---|---|
| | | | | | $S_p^o$ | $S_p^f$ | $\Delta S_p$ | |
| 01-09 | M8 1445 | 0.33 | 33.0 | 0.11 | 0.58 | 0.11 | 0.47 | 3.27 |
| | S1 1255 | 0.36 | 28.1 | 0.10 | 0.58 | 0.13 | 0.45 | 3.5 |
| 01-10 | S1 0108 | 0.38 | 36.2 | 0.14 | 0.58 | 0.08 | 0.50 | 2.57 |
| 01-11 | S1 0224 | 0.23 | 51.5 | 0.13 | 0.58 | 0.07 | 0.51 | 3.25 |
| | S1 0301 | 0.35 | 46.9 | 0.16 | 0.58 | 0.14 | 0.44 | 1.75 |
| | | | | | | | | $S_s/S_n$ Ave = 2.2 ± 1.66 |
| 03-01 | S12258 | 0.47, 0.23 | 26.6, 0.8 | 0.13 | 0.64 | 0.25 | 0.39 | 2.00 |
| | S1 2356 | 0.48, 0.13 | 26.2, 3.7 | 0.13 | 0.64 | 0.16 | 0.48 | 2.69 |
| | S1 0200 | 0.60, 0.22 | 20.1, 1.1 | 0.13 | 0.64 | 0.17 | 0.47 | 2.61 |
| 03-02 | S1 2213 | 0.42, 0.21 | 41.4, 6.3 | 0.19 | 0.64 | 0.19 | 0.45 | 1.37 |
| | S1 0015 | 0.45 | 41.3 | 0.19 | 0.64 | 0.22 | 0.42 | 1.21 |
| | S1 0119 | 0.45, 0.21 | 36.8, 4.1 | 0.18 | 0.64 | 0.19 | 0.45 | 1.50 |
| | S1 0335 | 0.52, 0.18 | 22.5, 3.8 | 0.13 | 0.64 | 0.15 | 0.49 | 2.77 |
| 03-03 | S1 0431 | 0.50, 0.14 | 36.0, 7.7 | 0.19 | 0.64 | 0.17 | 0.47 | 1.47 |
| | S1 0527 | 0.47, 0.22 | 33.0, 4.8 | 0.16 | 0.64 | 0.15 | 0.49 | 2.06 |
| | S1 0727 | 0.38, 0.31 | 27.5, 4.6 | 0.12 | 0.64 | 0.13 | 0.51 | 3.25 |
| | | | | | | | | $S_s/S_n$ Ave = 2.1 ± 0.71 |
| | | | | | | | | $S_s/S_n$ Cum Ave = 2.2 ± 1.45 |

* The ratio $S_s/S_n$ is computed as $(\Delta S_p - S_n)/S_n$.

Experiment 03 are 2.2 ±1.66 and 2.1 ±0.71, respectively; these values are statistically indistinguishable.

Collectively, the data presented in Table 14 indicate a product $S_s/S_n$ ratio of 2.2 which may be compared to the previously determined $S_s/S_n$ ratio of 1.5(5,11). The difference between these two values may be the result of incomplete $S_n$ recovery from the processed coal (leaving 0.04% $S_n$ on the coal or losing it during recovery would suffice for this experimentation), loss of $S_n$ during the recovery process (i.e., during vacuum drying), or a systematic error in any of the numerous analyses and measurements used in computation of the $S_s/S_n$ ratio such as original and final $S_p$, residue weight, purity, etc. Therefore, the higher product $S_s/S_n$ ratio obtained from $S_n$ recovery data is not considered to be reflective of process chemistry but of the increasing difficulty in obtaining an $S_n$ balance from low $S_p$ coal processing experiments.

A comparison of experiments performed with iron reagent (Experiment 01) and experiments performed with initially iron free reagent (Experiments 8, 9, and 03) indicates that reagent iron concentration does not effect the product $S_s/S_n$ ratio. This finding is in agreement with previously obtained bench scale data(5).

Most coal samples obtained during Experiment 03 were treated with two stages of toluene extraction rather than the nominal single stage extraction. Data from this experiment shows that 94 percent of the extracted $S_n$ was recovered in the first stage of extraction. Thus, approximately 0.01% w/w $S_n$ was recovered during the second toluene extraction of processed mine cleaned Martinka coal.

### 6.2.2.4 Process Effects on Coal Heat Content--

Mine cleaned Martinka feed coals and processed coals obtained from the RTU may be compared on the basis of mineral matter free (mmf) heat content to determine effects of the Meyers Process on the coal matrix. An mmf heat content was computed based on starting coal analyses and average processed coal analyses for each experiment using the Parr formula (ASTM designation D388-66). Results of these computations are presented in Table 15. These data indicate a mean heat content increase of 352 Btu per pound based on dry coal analyses; this corresponds to a 2.7% increase in coal heating value. On

TABLE 15. SUMMARY OF HEAT CONTENT CHANGES IN RTU PROCESSED COALS

| Experiment No. | Heat Content, Dry Basis, Btu/lb |  | Changes |  | Heat Content, Dry Mineral Matter Free Basis, Btu/lb |  | Changes |  |
|---|---|---|---|---|---|---|---|---|
|  | Initial | Final | Btu/lb | Percent | Initial | Final | Btu/lb | Percent |
| 8 (Shakedown) | 12508 | 12985 | 477 | 3.8 | 15172 | 15279 | 107 | 0.7 |
| 9 (Shakedown) | 12508 | 13213 | 705 | 5.6 | 15172 | 15260 | 88 | 0.6 |
| 01-01 | 12923 | 13397 | 474 | 3.7 | 15283 | 15459 | 176 | 1.1 |
| 01-02 | 12923 | 13300 | 377 | 2.9 | 15283 | 15508 | 225 | 1.5 |
| 01-03 | 12923 | 13268 | 345 | 2.7 | 15283 | 15396 | 113 | 0.7 |
| 01-05 | 12923 | 12888 | -35 | -0.3 | 15283 | 15185 | -98 | -0.6 |
| 01-06 | 12923 | 13163 | 240 | 1.9 | 15283 | 15264 | -19 | -0.1 |
| 01-07 | 12923 | 13123 | 200 | 1.5 | 15283 | 15337 | 54 | 0.3 |
| 01-09 | 12923 | 13487 | 566 | 4.4 | 15283 | 15255 | -28 | 0.2 |
| 01-10 | 12923 | 13158 | 235 | 1.8 | 15283 | 15426 | 143 | 0.9 |
| 01-11 | 12923 | 13071 | 148 | 1.1 | 15283 | 15367 | 84 | 0.5 |
| 03-01 | 12907 | 13258 | 351 | 2.7 | 15293 | 15420 | 127 | 0.8 |
| 03-02 | 12907 | 13388 | 481 | 3.7 | 15293 | 15393 | 100 | 0.7 |
| 03-03 | 12907 | 13265 | 358 | 2.8 | 15293 | 15342 | 49 | 0.3 |
| Average Heat Content Change |  |  | 352<br>±188 | 2.7<br>±1.5 |  |  | 80<br>±85 | 0.5<br>±0.5 |

a dry mmf basis a mean heat content increase of 80 Btu per pound is indicated (0.5% of the mmf heat content). The observed mmf heat content increase is not believed to be meaningful in the sense of coal upgrading but, rather, is considered to reflect inaccuracies associated with analyses and with the Parr formula itself. However, on the basis of these data, it appears reasonable to conclude that no measurable degradation of the coal matrix occurred during RTU L-R processing at temperatures of 230°F and 270°F with reagent iron concentrations of 0-4.5% w/w.

These data are in agreement with bench scale results indicating that the Meyers Process has little or no effect on the organic matrix of Appalachian bituminous coals. However, bench scale L-R experimentation performed with 14 mesh x 0 mine cleaned Martinka coal resulted in an mmf heat content loss of approximately 2% during 250°F processing for six hours or more. Thus, while no matrix oxidation was observed during L-R processing in the RTU, slight matrix oxidation was observed during bench scale L-R operation.

This discrepancy may be associated with coal weathering occurring during the 8-month period between obtaining a coal sample for bench scale processing and initiation of RTU coal processing. The unweathered coal (as indicated by the lack of sulfate sulfur) utilized during bench scale processing had an mmf heat content of 15,448 Btu per pound while that of the RTU feed coal was 15,249 Btu per pound (average of all three RTU feed coals). The 239 Btu per pound difference between bench scale and RTU feed coals represents 1.5% of the unweathered coals' mmf heat content. Thus, it is feasible that 1-2% of the coal organic matrix was oxidized during weathering and that this portion of the matrix is readily oxidizable by any oxygen bearing process. Data from the RTU would then indicate that no measurable coal oxidation can be further incurred during short periods of time under moderate conditions. It should be noted that if the preceding assumptions are correct, oxidation of 1-2% of the mmf coal is inevitable and will occur either during coal storage at the respective point of utilization or during coal processing.

### 6.2.3 Slurry Sampling

Slurry samples were drawn from each stage of T-2 and R-1 during RTU operation for the purpose of obtaining reagent Y data and coal analyses. Sampling ports in the RTU are located at two positions: (1) in the vessel wall below the slurry level and (2) in the slurry recirculation loop (R-1 only). Wall samples are taken by allowing slurry to pass through a ball valve into an evacuated sample bomb. One bomb is used to clear out stagnant coal which may accumulate in the sampling lines. The contents of this bomb are discarded and a second sample is immediately drawn for analysis. Loop samples are obtained from R-1 stages by full stream diversion of circulating slurry through a sampling tube which can be isolated and subsequently drained of slurry. Each sample drawn contained approximately one liter of slurry.

Coal analysis data obtained from slurry samples have been evaluated in conjunction with reagent Y data and the reaction model presented in Section 6.2.2. This treatment is limited to results from Experiment 01 since a pyrite leach rate expression is required. A plot of the difference between computed and analyzed $S_p$ values ($\Delta S_p$) versus sample location is presented in Figure 21. The sampling locations are spaced along the abscissa according to the theoretical time required to reach steady state compositions at each point. Data are presented at two times for most stages since two slightly different slurry residence times were utilized during Experiment 01. Data from wall samples and recirculation loop samples are indicated in the Figure by open and closed symbols, respectively.

Data from the three stages of mixing (T2-1, 2, and 3) indicate that coal samples from the first two stages contain significantly more pyrite than computed, while stage three samples are lower in pyrite than computed. Samples from the first two stages of T-2 were found to consistently contain more pyrite than the feed coal (1.4 ±0.66% w/w compared to a starting coal $S_p$ content of 0.58% w/w). Stage three mixer samples can be shown to be nonrepresentative and low in $S_p$ by using measured ferrous iron generation data. Measured $S_p$ values from R-1 wall samples are also seen to be low with respect to computed $S_p$ values although the $\Delta S_p$ approximated analytical precision after the first stage of pressurized processing. The limited data from R-1 loop samples are generally consistent with wall sampling data although high measured pyrite values were obtained from R1-3 samples at 270°F.

These data suggest major segregation of the feed coal prior to reagent reflux in the third stage of mixing. Bench scale experimentation performed to determine causes of coal slurry foaming has indicated that reagent reflux is key to effective coal wetting at atmospheric pressure(11). Hence, high pyrite coal appears to segregate in the lower portion of T-2 (the vicinity

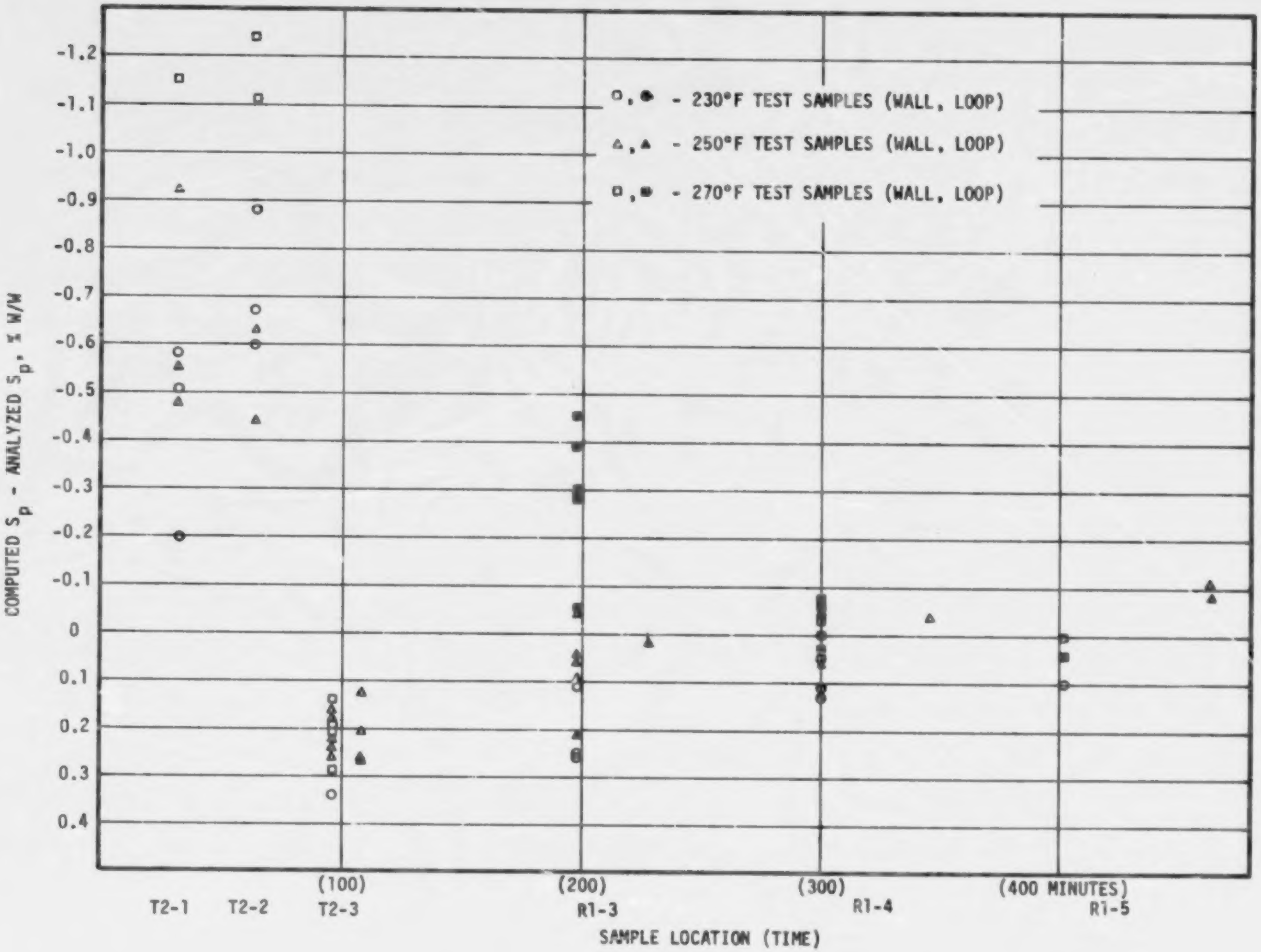

Figure 21. Summary of Estimated Sampling Bias

of the sampling ports) prior to effective coal wetting. The reverse segregation effect (drawing low pyrite samples rather than high pyrite samples) observed in the third stage of mixing is not understood, but may be associated with a froth flotation effect caused by reagent boiling and the injection of steam. This phenomena is also observed in R-1 where both oxygen and steam are injected into the slurry.

The apparent reduction of sampling bias to the level of analytical precision during the last two stages of R-1 processing probably relates to the fact that the $S_p$ contents of all size-gravity coal fractions are very low. That is, non-representative sampling of a depyritized coal is not likely to yield samples having substantially different $S_p$ contents from the mean $S_p$ content of the whole coal.

Coal segregation indicated by $\Delta S_p$ data is verified by slurry solids content data which are summarized in Figure 22. Slurry solids data from each sampling location are presented in the Figure as a function of $\Delta S_p$. The nominal solids content of the feed slurry was 33% for all conditions of Experiment 01 and dilution down to approximately 29% was effected by the addition of live steam for heating. Slurry solids data indicate that samples which were high in $S_p$ (i.e., samples from T2-1, T2-2, and the R1-3 loop) also tended to be solids rich with respect to the feed slurry. On the other hand, samples which were low in $S_p$ tended to have reasonable or slightly low slurry solids contents. Thus, as would be expected, whether or not a slurry sample contains coal which is representative of the whole coal is reflected in the solids content of the sample. If the sample slurry solids content is not representative of the system as a whole, the coal contained in the sample probably is not representative of the whole coal either.

Despite the fact that slurry samples drawn from the RTU were biased with respect to $S_p$ and solids contents, reasonably good sampling precision was obtained. Replicate sampling generally yielded $S_p$ agreement to within ±0.07% w/w, $S_s$ agreement to within ±0.03% w/w and slurry solids agreement to within ±3%. Such precision coupled with sampling bias data would tend to indicate that only specific slurry streams or eddys are accessible through specific sampling ports and that the composition of the accessible slurry did not change significantly with time. Thus, improvement of slurry sampling most

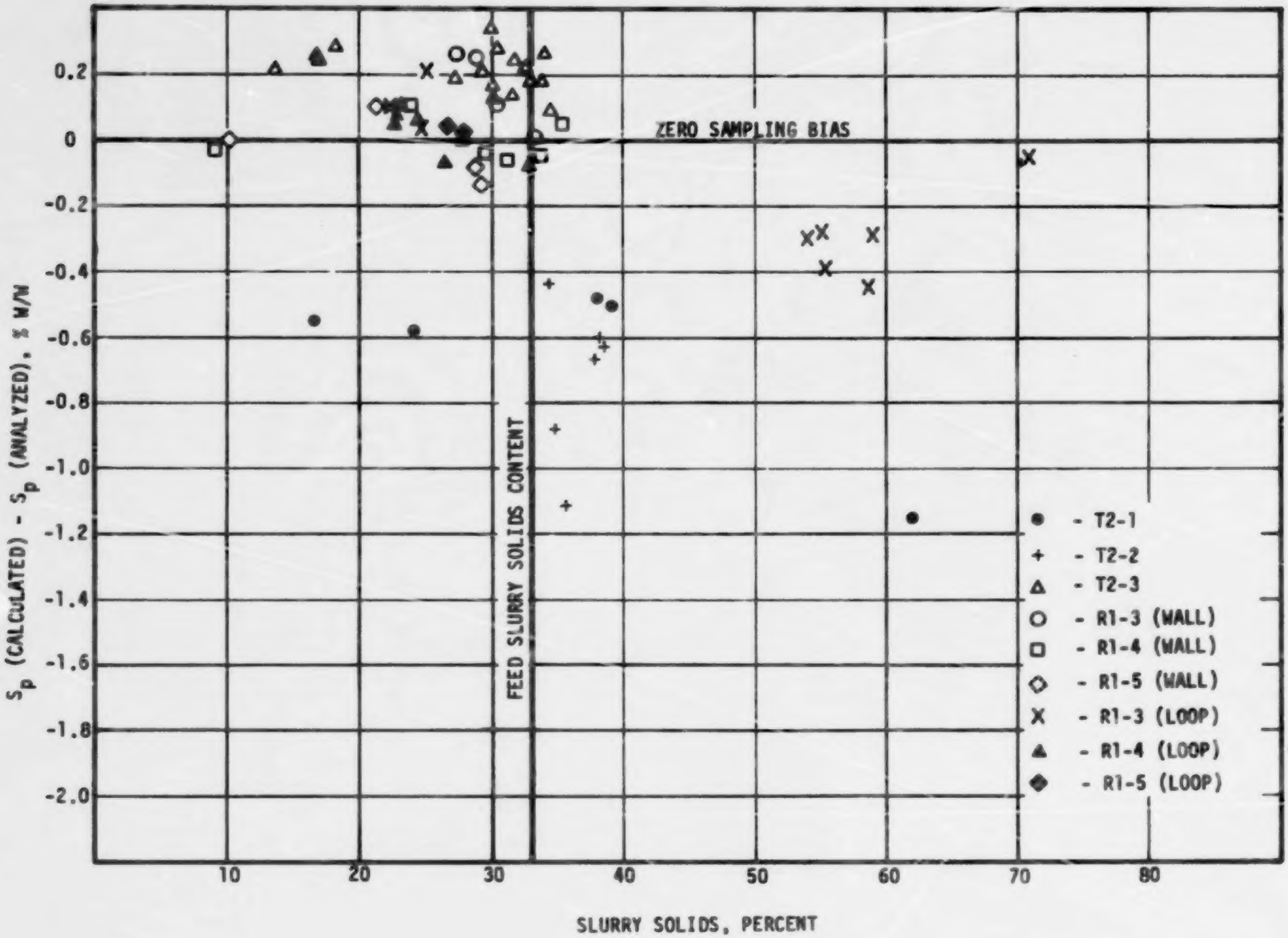

Figure 22. Slurry Concentration Variation as a Function of Sample Location

likely requires more efficient slurry agitation within the various stages and/or relocation of the sampling ports away from localized flow patterns (i.e., wall effects).

### 6.2.4 RTU Mass Balance Data

Flow rates of RTU process streams were monitored wherever possible to enable mass balance determinations to be made around each of the major unit operations, namely coal-reagent mixing, pyrite reaction and slurry filtration. Primary flow measurement equipment utilized in the RTU to facilitate plant operation and provide mass balance data were: (1) a weigh belt for metering ground coal to the system, (2) magnetic flow meters for measuring liquid and slurry flow rates, (3) rotameters for measuring steam, oxygen and wash water flow rates and (4) target meters for measuring oxygen feed and exhaust flow rates. Output from the primary flow measurement equipment was generally dependent upon the input of one or more auxiliary devices which provide such data as stream temperature, pressure, gas purity, etc. The majority of this data was recorded at 3-minute intervals by the Doric data logger although some data were recorded manually (i.e., steam and wash water feed rates) at intervals commensurate with the data reduction needs.

With the exception of the magnetic flow meters, all primary flow measurement devices used in the RTU measured mass flow directly. The weight belt meters the coal feed utilizing a load cell which measures the weight of coal per unit area of belt. Output from the weigh belt is transmitted as total coal weight and also as a feed rate. Calibration can be obtained through direct weighing of the belt effluent. Rotameters and target meters are essentially momentum measurement devices which may be calibrated at either standard conditions or operating conditions; the former requires the application of temperature and pressure corrections. However, magnetic flow meters are true velocity meters and, as such, yield accurate volumetric flow rates. In order to convert from the magnetic flow meter volumetric flow to mass flow, a general slurry density expression was formulated in terms of temperature, total iron sulfate concentration, acid concentration and slurry solids content. Considering the liquid reagent components as ideal solutions and neglecting the specific volume of dissolved salt, the slurry density was expressed as:

$$\rho = \frac{100 + \dfrac{S}{1 - 0.01S}}{\left[\dfrac{100 - (A + 3.578\ TFe)}{62.248} + \dfrac{A}{113.966}\right]\left[1 + 0.0003(T - 77)\right] + \dfrac{S}{84(1 - 0.01S)}}$$

where

$\rho$ is the slurry density, lb/ft$^3$,

A is the sulfuric acid concentration of the reagent, wt. %,

TFe is the total iron concentration of the reagent, wt. %,

S is the slurry solids content, wt. %, and

T is the slurry temperature, $^{o}$F.

The densities of water and sulfuric acid at 77$^{o}$F (25$^{o}$C) were taken to be 62.25 and 113.97 lb/ft$^3$, respectively. A value of 84 lb/ft$^3$ was used for the density of the coal.

This expression yields density estimates which agree with measured values to within about 5% or less for the solutions used in the RTU. Hence, the precision of mass flow rates obtained from magnetic flow meters is approximately 5% rather than the 0.5-1% precision associated with volumetric flow readings.

Mass flow rates which are of importance to mass balance efforts, but are not measurable by primary flow measurement equipment, include the steam flash rate from R-1 pressure let-down, slurry accumulation or depletion in T-2 and R-1, and the flow rate of wet product coal cake from the S-1 filter. These quantities were either inferred from the other data normally obtained from the RTU or obtained by special measurement during specified experimentation. The quantity of steam flashed during R-1 pressure let-down can be estimated from the increase in the temperature of vent gas scrubber water in T-4. Thus, assuming perfect scrubber efficiency, the mass flow rate of flash steam was calculated from the flow rate of scrubber water and its temperature change resulting from steam condensation. Slurry accumulation or depletion in T-2 and R-1 is computed from slurry level data generated by sensors located in the last stage of each vessel. Special measurements are required to obtain the mass flow rate of wet coal cake from S-1. This involves collecting the S-1 solid effluent in a tared dumpster and determining weight increases as a function of time. This procedure is both time consuming and cumbersome and was performed only for special mass balance experimentation. Thus, mass balances around S-1 were not generally performed.

Computer programs which are presented in Volume II, Appendix A were written to perform mass balances around T-2 and R-1. These programs account for all process streams and utilize both Doric data and manually recorded data. Data from Experiment 10 (a special shakedown mass balance test), Experiment 01 and Experiment 03 were evaluated with the aid of these programs to identify inconsistencies among the RTU flow measurement outputs.

A low temperature and pressure test (Experiment No. 10) was performed during RTU shakedown to obtain a complete system mass balance and verify the major flow measurement devices. This experiment was performed with a water-coal slurry using flow rates of 3 gpm and 500 lb. of coal per hour. These flow rates correspond to residence times of approximately 0.6 hour in the mixer and 3.2 hours in the reactor (all five stages of R-1 were utilized). Mixer heating was utilized to maintain the slurry at $190^0$F (sufficiently hot for proper P-1 operation but below the solution boiling point). Slurry temperatures in R-1 were allowed to drop in order to minimize evaporative losses during pressure let-down. The plant was operated for 10 hours under the nominal conditions with the last 3 hours being considered to be at steady state.

The solids balance between the A-3 plant coal feed and S-1 filter belt output indicates that 160 lb. of dry coal was "lost". This represents 11% of the feed coal. However, filter belt flooding conditions prevailed during the entire steady state operational period and solids removed during the belt wash were discarded to T-9 rather than being returned to the filter cake as a filter belt wash water slurry per normal operation. Post-run observation indicated that a "large build-up of coal" was found in the filter belt drip pan. Thus, the 160 lb. coal "loss" appears to be a reasonable and explainable occurrence.

The overall liquid balance included units A-3, T-2, R-1, T-5 and S-1. The vent steam could not be computed since the $\Delta T$ of T-4 scrubber water was not measured. The vent steam from T-2 (operating at $190^0$F) was assumed to be negligible while the steam from R-1 (operating at $\sim 160^0$F) was computed to to be negligible on the basis of inlet and outlet reagent temperature values from the knockout drum V-1. This balance indicated an 830 lb. liquid gain (17% of input liquids). This result may be partially or totally due to the following: (1) error in reagent filtrate flow rates, which, for this experiment, were both FE-157 and FE-158, or (2) leakage from water flushed pump and mixer seals. The possibility of incorrect reagent feed flow rates has been discarded since a good mass balance was obtained around the T-2 mixer. These data combine to yield the total system mass balance which includes units A-3, T-2, R-1, T-5 and S-1. The net result is a 662 lb. gain which represents 11% of the input material.

A mass balance around T-2 based on coal, reagent and steam feed rates and slurry flow calibrations of FE-29 (slurry out) resulted in a total mass balance of better than 93%. This result appeared to be reasonable since the accuracy of each of the two magnetic flow meters is estimated to be approximately 5%. A heat balance around T-2 essentially verified the validity of FI-16/18 steam flow indicators. A mass balance around the combined units T-2 and R-1 indicated a loss of 1755 lb. (28% of the input material). This result was found to be caused by improper operation of the R-1 outlet slurry flow meter (FE-60). Subsequent experimentation revealed that signal response times of some magnetic flow meter components were sufficiently slow compared to slurry pulse flow times (pulse lengths are generally less than two seconds) that entire pulses were sometimes not detected. Attempts were made to resolve this response problem throughout Experiment 01. However, satisfactory performance of FE-60 was never obtained during pulse flow operation and the flow meter was ultimately removed from service.

Data from the Experiment 10 mass balance test gave rise to the following observations:

- Stream flow measurement equipment associated with T-2 was operational and accurate. Subsequent experimentation indicated that steam flow meters FI-16 through 18 were somewhat undersized which necessitated frequent use of flow meter bypass lines to maintain desired T-2 temperatures. Thus, under normal operating conditions, steam feed rates to T-2 were not accurately known at all times.

- Magnetic flow meters could not be utilized under conditions of pulse flow. Thus, the quantity of slurry leaving R-1 and entering S-1 could not be directly measured with available flow measurement equipment. Although the mass flow rate of slurry from R-1 can in principle be estimated from the increase in temperature of T-4 scrubber water, adequate monitoring of scrubber water temperatures was never achieved during RTU operation. As such, mass balances could not be performed on either R-1 or S-1 with available data.

- An accurate accounting of system solids cannot be made unless the S-1 filter belt is operating properly. Filter belt operation under flooding or near flooding conditions necessitates discard of the belt wash solution and its entrained coal component.

Experimentation performed in the RTU did provide meaningful mass balance data relating to the T-2 mixing unit. Results of the T-2 mass balances from RTU experimentation are presented in Table 16. The first two columns of the table list the experiment number and day. The second two columns list the run times included in the mass balance. These times do not necessarily reflect actual experimental run times since periods of time which included data noise on one or more of the required data channels have been eliminated. The remaining columns in Table 16 list mass balance data for each experiment. The accumulation column lists material "gains" or "losses" associated with slurry level changes within T-2. Slurry level data from Experiment 01 was recorded manually and, therefore, in limited quantity; available data is insufficient to permit computation of material accumulation. During Experiment 03 the slurry level of T-2 was recorded by the Doric Data Logger and included in the mass balance. The accumulation term is generally seen to be small as would be expected since every effort was made to maintain a constant slurry level throughout each experiment.

Data presented in Table 16 indicate that a good material balance was obtained for the T-2 unit. An average recovery of 100% was obtained and most experiments balanced to within 7%. Thus, the precision obtained in mass balancing the T-2 unit is comparable to that of the flow meters monitoring the liquid flow streams. The trend from slightly low material recovery to slightly high material recovery during the period of RTU operation may relate to instrument calibration drift or an interaction between magnetic flow meter electrodes and the leach reagent during the course of experimentation (i.e., scaling or corrosion). However, iron concentration, in this case, should have no effect on the magnetic flow meter calibration; that this is correct is evidenced by

## TABLE 16. T-2 MASS BALANCE DATA FROM RTU PROCESSING EXPERIMENTATION

| Experiment No. | Day | Mass Balance Time | | Material In, lbs. | | | | Material out, lbs | Accum.* | Total out, lbs | Gain, lbs | Percent Recovery |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Start | Stop | Coal | Reagent | Steam | Total | | | | | |
| 10 (Shakedown) | 250 | 20:59 | 23:56 | 1468 | 4317 | 150 | 5935 | 5609 | -74 | 5535 | -400 | 93 |
| 01-01 | 299 | 16:36 | 02:57 | 3080 | 6195 | 288 | 9563 | 9369 | DATA NOT AVAILABLE | 9369 | -194 | 98 |
| 01-02 | 300 | 03:03 | 09:00 | 1770 | 3565 | 165 | 5500 | 5185 | | 5185 | -315 | 94 |
| 01-03 | 305 | 10:02 | 15:29 | 1621 | 3089 | 151 | 4861 | 4656 | | 4656 | -205 | 96 |
| | | 16:26 | 21:29 | 1506 | 2871 | 140 | 4517 | 4252 | | 4252 | -265 | 94 |
| 01-04 | 305 | 21:32 | 23:29 | 580 | 1108 | 54 | 1742 | 1781 | | 1781 | 39 | 102 |
| 01-06 | 306 | 00:02 | 10:38 | 3139 | 5976 | 293 | 9408 | 9307 | | 9307 | -101 | 99 |
| 01-05 | 314 | 12:31 | 13:48 | 388 | 732 | 40 | 1160 | 1019 | | 1019 | -141 | 88 |
| | | 15:52 | 16:46 | 272 | 519 | 27 | 818 | 807 | | 8 7 | - 11 | 99 |
| | | 17:22 | 01:13 | 2327 | 4519 | 238 | 7084 | 6892 | | 6892 | -192 | 97 |
| 01-07 | 319 | 22:18 | 00:48 | 745 | 1394 | 70 | 2209 | 2215 | | 2215 | 6 | 100 |
| | 321 | 17:00 | 02:18 | 2718 | 4974 | 129 | 7821 | 7840 | | 7840 | 19 | 100 |
| 01-08 | 322 | 02:51 | 04:48 | 580 | 1056 | 27 | 1663 | 1663 | | 1663 | 0 | 100 |
| 01-09 | 322 | 04:51 | 13:48 | 2663 | 4797 | 124 | 7584 | 7741 | | 7741 | 157 | 102 |
| 01-10 | 322 | 13:51 | 01:48 | 3557 | 6366 | 106 | 10029 | 10492 | | 10492 | 463 | 105 |
| 01-11 | 325 | 17:31 | 02:58 | 2620 | 7739 | 131 | 10690 | 8535 | | 8535 | -2155 | 80 |
| 03-01 | 6 | 17:40 | 01:58 | 2469 | 7651 | 569 | 10689 | 11267 | 279 | 11546 | 857 | 108 |
| 03-02 | 9 | 12:02 | 19:14 | 1430 | 4174 | 500 | 6104 | 6533 | -64 | 6469 | 365 | 106 |
| | | 20:05 | 21:14 | 228 | 666 | 80 | 974 | 1123 | -20 | 1103 | 129 | 113 |
| | | 21:38 | 03:23 | 1145 | 3304 | 399 | 4848 | 5160 | 55 | 5215 | 367 | 107 |
| 03-02 | 10 | 17:10 | 07:28 | 2852 | 8313 | 1012 | 12177 | 13350 | 62 | 13412 | 1235 | 110 |

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* Material accumulated in the mixer.

the fact that Experiment 10 was performed with pure water and still indicates a slightly low material recovery as do nearly all early experiments.

An oxygen mass balance around R-1 for an actual coal processing experiment requires the following data: (1) oxygen flow rates into R-1, (2) V-1 vent gas flow rates, (3) the oxygen content of V-1 vent gas, (4) $Fe^{+2}$ generation rates from both pyrite reaction and matrix oxidation, (5) starting and final $Fe^{+2}$ concentrations for each reaction stage, and (6) inlet and outlet reagent $Fe^{+2}$ concentrations. Since the oxygen mass balance is reflective of both the instrument and analytical precisions as well as either inferred or extrapolated data (i.e., excess $Fe^{+2}$ generation rates), an accurate oxygen balance of a coal processing experiment is not readily obtained. However, an effort was made to perform oxygen balances for all experimentation performed in the RTU.

Estimates of the average oxygen consumption rates during processing were made based on pyrite removal data and excess $Fe^{+2}$ generation rates presented in Section 6.2.2 and on reagent Y data. These values are compared to oxygen consumption values indicated from oxygen flow data and R-1 pressure data in Table 17. Experimental conditions and run times are reiterated in the first five columns of the table. Values of total input and vent oxygen obtained by integrating the output of FE-61 and FE-44 are listed in columns six and seven. Quantities of oxygen accumulated or depleted in R-1 as indicated by starting and final reactor pressures are listed in column eight. The difference between oxygen input (column six) and the sum of vent oxygen and oxygen accumulated in the reactor (columns seven and eight) is the oxygen consumption indicated by RTU flow and pressure equipment and is listed in column nine. The average measured oxygen consumption rate for each experiment (listed in column ten) may be compared to the average oxygen consumption rates computed from $\Delta S_p$ and excess $Fe^{+2}$ data (listed in column eleven) to indicate the validity of acquired mass balance data.

Data presented in Table 17 show little correlation between measured and computed oxygen consumption values. The observed discrepancies do not appear to be associated with the estimated excess $Fe^{+2}$ generation rates since estimation errors of this type should result in comparable differences between measured and computed oxygen consumptions for experiments performed at similar

## TABLE 17. OXYGEN MASS BALANCE DATA OBTAINED DURING RTU EXPERIMENTATION

| Experiment No. | Temp. °F | $P_{O_2}$, psia | $O_2$ Feed Rate SCFH | Run Time, Hrs | Oxygen, SCF |  |  |  | Average $O_2$ Consumption Rate, SCFH |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | In | Out | Accum. | Consumed | Measured | Computed |
| 01-01 | 230 | 22 | 56 | 9.7 | 541 | 543 | 27 | -29 | -3 | 9 |
| 01-02 | 231 | 49 | 57 | 6.9 | 395 | 128 | 2 | 265 | 38 | 9 |
| 01-03 | 251 | 39 | 54 | 11.5 | 21 | 178 | 11 | 432 | 38 | 18 |
| 01-04 | 251 | 39 | 59 | 1.9 | 113 | 28 | -2 | 87 | 43 | 18 |
| 01-05 | 250 | 25-39 | NA | 10.2 | -------------------- DATA NOT AVAILABLE -------------------- |  |  |  |  |  |
| 01-06 | 251 | 52 | 123 | 10.7 | 1318 | 911 | -3 | 410 | 38 | 23 |
| 01-07 | 245 | 10-53 | 59 | 9.5 | 557 | 172 | 36 | 349 | 37 | 14 |
| 01-08 | 245 | 50 | 57 | 1.9 | 109 | 9 | -3 | 103 | 51 | 14 |
| 01-09 | 270 | 49 | 56 | 8.5 | 479 | 0 | 7 | 472 | 55 | 27 |
| 01-10 | 270 | 23 | 56 | 12.3 | 693 | 594 | 3 | 96 | 8 | 20 |
| 01-11 | 251 | 52 | 128 | 11.5 | 1478 | 1133 | -4 | 349 | 30 | 21 |
| 03-01 | 222 | 28 | 94 | 10.1 | 909 | 953 | -42 | -2 | 0 | 15 |
| 03-02 | 232 | 34 | 88 | 15.3 | 1200 | 1085 | 5 | 110 | 7 | 15 |
| 03-03 | 234 | 33 | 150 | 14.3 | 2254 | 3189 | 9 | -944 | -66 | 22 |

temperatures. Results from Experiments 01-01 and 01-02, 01-09 and 01-10, and 03-02 and 03-03 do not indicate that this is the case.

Oxygen accumulation quantities are not sufficiently large to have a significant impact on the measured consumption rates and therefore do not represent a major source of error. Oxygen feed rates measured with FE-61 should be accurate since meter calibration was performed under conditions identical to those used during plant operation and rough flow rate verification is provided by downstream rotameters used to proportion oxygen among the reactor stages (F1-62 through F1-66). Thus, the most probable source of the observed discrepancy appears to be the vent oxygen flow rate measurement.

The rate at which oxygen is vented from V-1 is computed from the vent gas oxygen content indicated by AE-171 and flow rate indicated by FE-44. The oxygen analyzer provides continuous analysis of a dried slipstream of the V-1 discharge gas. Analyses from AE-171 cannot be wholly responsible for observed discrepancies since to bring Experiments 01-02 through 01-09 and 01-11 into agreement with computed consumption rates would require stream oxygen purities greater than 100%. However, there are reasons why FE-44 may be singly responsible for observed data discrepancies:

- Water saturated vent gas was cooled or in the process of cooling when its flow rate was being measured. Thus, entrained water droplets or condensate may have contacted the flow target and thereby altered the meter performance. This possibility can be eliminated during future experimentation by locating the flow meter in a heated region with a large cross section to prevent condensation and to decrease the likelihood of entrainment.
- Owing to the pressure regulator used in the RTU, reactor venting was often pulsed rather than continuous. Pulses occurring during venting were up to approximately 9 minutes in duration and had amplitudes ranging to nearly 400 SCFH. Since the data logger was recording at 3-minute intervals, true pulse shapes are not known and the possibility exists that entire pulses were not detected. It should be noted however that venting during Experiments 01-03, 01-09, 01-10, 01-11 and 03-03 was reasonably smooth and pulse free. Yet, data from these experiments do not correspond to computed oxygen consumption estimates.

It therefore appears that an additional design effort is required in conjunction with further elevated temperature processing experimentation performed in the absence of coal to resolve the problems associated with obtaining a balance of oxygen in the RTU. Additional bench scale tests are also required to define excess $Fe^{+2}$ generation rates at temperatures above 212°F.

## 6.3 DATA ANALYSIS CONCLUSIONS

1. Three distinct coal samples (coal Nos. 1, 2 and 3) were supplied by American Electric and Power for coal processing experimentation in the RTU. These coals differed with respect to coal ash, heat content, total sulfur, and sulfur forms analyses.

2. RTU processing times required to attain steady state operation with respect to reagent Y can be substantially larger than would be estimated by this ratio of reactor volume-to-volumetric slurry flow rate. However, since product coal $S_p$ contents are relatively insensitive to small changes in reagent Y (particularly when $S_p$ is reduced to 0.2% w/w or less), a plug flow type estimate of time required to achieve steady state appears to be effective with respect to product coal $S_p$ contents.

3. All RTU processing experiments performed with 14 mesh top-size mine cleaned Martinka coal and acidified iron reagent at temperatures above 230°F yielded product coals having $S_p$ contents of 0.13% w/w to 0.19% w/w after nominal residence times of 5 to 6 hours. Similar processing at 230°F yielded product coals with $S_p$ contents of 0.24% w/w.

4. RTU coal processing experiments performed with acidified iron sulfate reagent reduced coal sulfate sulfur from 0.34% w/w to approximately 0.12% w/w after application of a preliminary filter belt wash followed by the standard laboratory washing and work-up. Coal processing with acidified iron free reagent reduced coal sulfate sulfur from 0.31% w/w to approximately 0.02% w/w after a filter belt wash and standard laboratory work-up.

5. Little or no excess ash removal was observed during RTU processing of mine cleaned Martinka coal. Ash depletion from the coal generally corresponded directly to the quantity of pyrite and sulfate removed during processing.

6. Coal processing data obtained from the RTU was correlatable with the previously determined leach rate expression, namely:

$$r_L = K_L Y^2 W_p^2$$

where

$K_L$ is the leach reaction rate constant

Y is the ratio of reagent ferric ion-to-total iron concentration, and

$W_p$ is the weight percent of pyrite in the coal.

7. Coal desulfurization rates in the RTU exhibited an Arrhenius type exponential temperature dependence as did previous bench-scale experimentation. That is,

$$K_L = A_L \exp [-E_L/RT]$$

where

$A_L$ is the pre-exponential factor or frequency factor

$E_L$ is the activation energy

R is the gas constant, and

T is the reaction temperature.

However, rate constants $K_L$ observed during RTU processing were 3 to 8 times greater than those obtained during bench-scale experimentation. This is attributed in part to non-ideal mixing of the reaction system which is a series of continuous flow stirred tank reactors.

8. Desulfurization rates obtained during coal processing with acidified water reagent appear to be essentially the same as those obtained by processing with acidified iron sulfate reagent. Thus, reagent iron concentration does not affect pyrite leach rates with acidified reagents.

9. Mine cleaned Martinka coal can be processed through the RTU to yield a product coal having less than 0.6 pound of sulfur per $10^6$ Btu.

10. Reagent regeneration in the RTU appeared to be adequately described by the previously determined regeneration rate expression:

$$r_R = K_R P_{O_2} (Fe^{+2})^2$$

where

$K_R$ is an Arrhenius type rate constant

$P_{O_2}$ is the oxygen partial pressure

$Fe^{+2}$ is the concentration of ferrous ion in reagent.

The reagent regeneration rate constant obtained in the RTU appeared to be at least 37% of the rate constant obtained at bench-scale. This possible disparity may be the result of relatively rapid disentrainment of oxygen bubbles from the slurry and the fact that the regenerator volume (slurry recirculation loop volume) per unit volume slurry is lower in the RTU than in the bench-scale unit.

11. Reagent regeneration rates could not be improved by increasing the oxygen throughput from a fourfold to a fourteenfold stoichiometric excess.

12. Excess ferric ion consumption appears to be a temperature dependent phenomenon. The degree to which this dependence is quantified will determine the precision with which reagent regeneration rates can be measured during L-R processing of low pyrite coals (i.e., the mine cleaned Martinka coal).

13. An average dry mmf heat content increase of 80 Btu per pound (±85 Btu per pound) was obtained during L-R coal processing of 14 mesh top-size mine cleaned Martinka coal in the RTU at temperatures of 230° to 270°F with 0 to 4.5% w/w iron reagent. Thus, no coal matrix degradation was observed during RTU coal processing.

14. RTU coal processing experimentation performed with acidified reagents having 0 to 4.5% w/w total iron concentrations indicated a product sulfate sulfur-to-elemental sulfur ratio of 2.2. Because of inefficiencies associated with the recovery of small quantities of elemental sulfur (less than 0.3% w/w) and physical losses which may be incurred, this data is considered to be essentially in agreement with previous bench-scale data indicating a 1.5 product sulfur ratio. Thus, reagent total iron concentration did not appear to affect the ratio of sulfur products during RTU operation.

15. Slurry sampling during RTU operation was generally of high precision but was not representative of the bulk slurry. It, therefore, appears that meaningful slurry sampling will require more efficient slurry agitation and/or relocation of the sampling ports away from areas subject to localized flow patterns, such as wall effects and eddys.

16. Magnetic flow meters are not suitable for measurement of slurry flow rates under pulse flow conditions encountered

in the R-1 effluent. To obtain a material balance of the R-1 unit will require an alternate flow measurement device with faster response times or an estimation of slurry effluent from the quantity of steam flashed during R-1 pressure let-down.

17. An excellent material balance was obtained for the mixer T-2 with an average material recovery of 100% being obtained. Material balance precision was approximately 7% which is comparable to the precision of flow meters used to monitor the liquid flow streams.

18. The acquisition of an oxygen mass balance for the R-1 unit appears to require modification of the vent gas flow measurement system.

# 7. SUPPORTING BENCH-SCALE EXPERIMENTATION

## 7.1 INTRODUCTION

Supporting bench-scale experimentation has been conducted concurrent with the RTU program to expand coal cleaning technology utilizing the Meyers Process and to assist on-line RTU operations by supplying technical processing data to assist in the overall program.

This section principally contains experimental work involving the use of the Meyers Process reagent for gravity separation of coal prior to chemical cleaning as well as a review of related studies performed earlier in the U.S.S.R.

Included in the section are experimental studies examining gravity separation of coal under equilibrium and non-equilibrium conditions and their attendant effect upon recovery of clean coal fractions.

Additional experimental studies are presented herein which include: (1) chemical processing (Meyers Process) of sink fractions of gravity separated coal; (2) comparisons with studies made in the U.S.S.R.; and (3) general experimentation to investigate processing changes, weathering of coal, density determination of coal slurries, and elemental sulfur recovery by acetone.

## 7.2 GRAVICHEM SEPARATION

### 7.2.1 Background

A practical method for actual float-sink cleaning of coal in a dense liquid has long been sought as an alternative to mechanical cleaning. Heavy liquids, such as zinc chloride-water, or chlorinated, brominated, or fluorinated hydrocarbons are useful for prediction of yields which can theoretically be obtained in mechanical washing plants, but are impractical for actual production because they are expensive and add pollutants to the coal, atmosphere or water table. We find that the density of aqueous ferric sulfate leach solution, as utilized in the Meyers Process, is ideal for accomplishing a practical gravity separation of coal for specific gravities between 1.2 and 1.4. For example, for about 40% of Appalachian coal, the float coal (which is often 40-60% by weight of the total) averages 0.8-1.2 lbs $SO_2/10^6$ Btu and needs no further processing to meet standards, while the sink coal slurry contains most of the coal pyrite. This sink slurry can then be processed through the Meyers Process to produce coal containing 1.2-1.5 $SO_2/10^6$ Btu. This approach allows production of coal which will meet $SO_x$ emissions standards for both new and existing stationary sources, and reduces processing costs relative to the straight through Meyers Process by allowing 40-60% of the coal to bypass reactor, elemental sulfur extraction and dryer units. This float-sink approach was tested many years ago by A.Z. Yurovskii in the U.S.S.R. but only published in the open literature very recently(12). Yurovskii subsequently treated the sink coal with a mixture of nitric acid and ferric sulfate to remove pyritic sulfur, not realizing that the separation medium itself was sufficiently active to accomplish near total pyritic sulfur removal.

### 7.2.1.1 Literature Background--

The cited work of Yurovskii reports laboratory (bench-scale) work for the removal of iron pyrite ($FeS_2$) from coal by reacting it with ferric sulfate solutions under a variety of conditions, and scale-up studies at pilot plant level which demonstrates ferric sulfate solution gravity separation using centrifugal separators with simultaneous sulfur and ash reduction. Principally, he investigated the effects of temperature, multiple ferric sulfate treatments and ash content on the degree of pyrite removal. His data support the observations from Gravichem processing (Sections 7.2.2 and 7.2.3) that significant reduction in ash content and pyrite is observed upon preliminary or sustained treatment of coal with ferric sulfate solution. Yurovskii, however, only reported 43% removal as his highest value for pyrite depletion in his bench-scale studies after twofold one-hour desulfurizations, which is low when compared to the Meyers Process. Yurovskii's work is discussed in more detail in Section 7.2.2 and 7.2.3.

### 7.2.1.2 Process Application--

The Gravichem variation of the Meyers Process involves utilization of ferric sulfate leach solution to gravity separate input coal into a very low pyrite float material and a high pyrite sink material. The sink material is subsequently heated to reaction temperature and processed through the Meyers Process. The Gravichem process modification is shown schematically in Figure 23. Run-of-mine coal, often containing 5-10 lbs $SO_2$/MM Btu, is crushed and screened to remove rock and easily removed pyrite. This rough-cleaned coal is mixed with leach solution and pumped to a tank, where coal lighter than the selected specific gravity of the leach solution floats and the heavier coal sinks. The float fraction is filtered and washed but not dried, while the sink fraction is treated by the Meyers Process to give a dry coal product. The processed-sink fraction may be hot-briquetted without binder (see Figure 24) to give a near 0% moisture product suitable for shipping in an open hopper-car. For stoker-boiler (industrial-type boiler) applications, it may be recombined with the wet float coal filter cake (about 20% moisture) to give a combined product of a shippable 1" x 0 grind with a combined moisture content of 10%.

### 7.2.2 Equilibrium Gravichem Separation

A series of float-sink separations of Martinka mine coal (14 mesh x 0) in ferric sulfate leach solution of varying specific gravity were performed (Table 18) which demonstrate the feasibility and the physical and chemical basis of the Gravichem concept.

These tests were of an equilibrium type in which coal was mixed with hot leach solution ($80^{o}C$) in an agitator for 15 minutes to ensure wetting, then transferred to a float sink apparatus maintained at $80^{o}C$ (Figure 25) and allowed to separate without stirring. After the specified times, the float product was skimmed from the top of the vessel and the sink product was separated from the remaining leach solution. The results (Table 18) show that float coal is obtained in 23-48% w/w yield, in each case meeting the NSPS standard of 1.2 lbs $SO_2/10^6$ Btu — i.e., 0.94-1.16 lbs $SO_2/10^6$ Btu, while the sink fraction treated by the Meyers Process gave a product of about 1.2-1.3 lbs $SO_2/10^6$ Btu.

The first separation (Experiment 1 of Table 18) was performed utilizing a standard mixed organic solvent of specific gravity 1.30 for purposes of comparison with leach solution gravity separations (Experiments 2-7). It can be seen that the yield of leach-solution float at 1.28 specific gravity was equivalent to that obtained with the organic solvent, indicating that the flotation utilizing ferric sulfate leach solution is essentially a physical separation

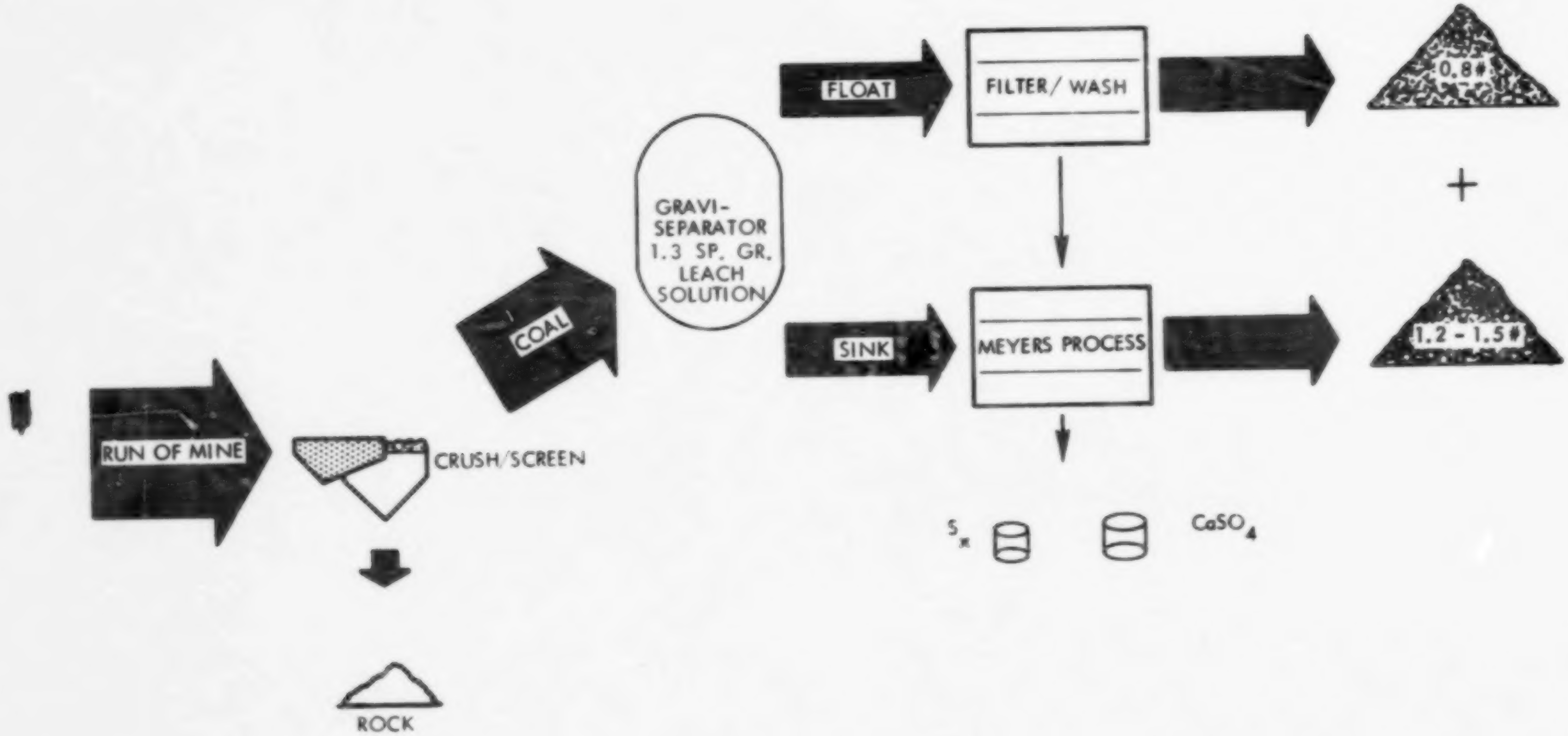
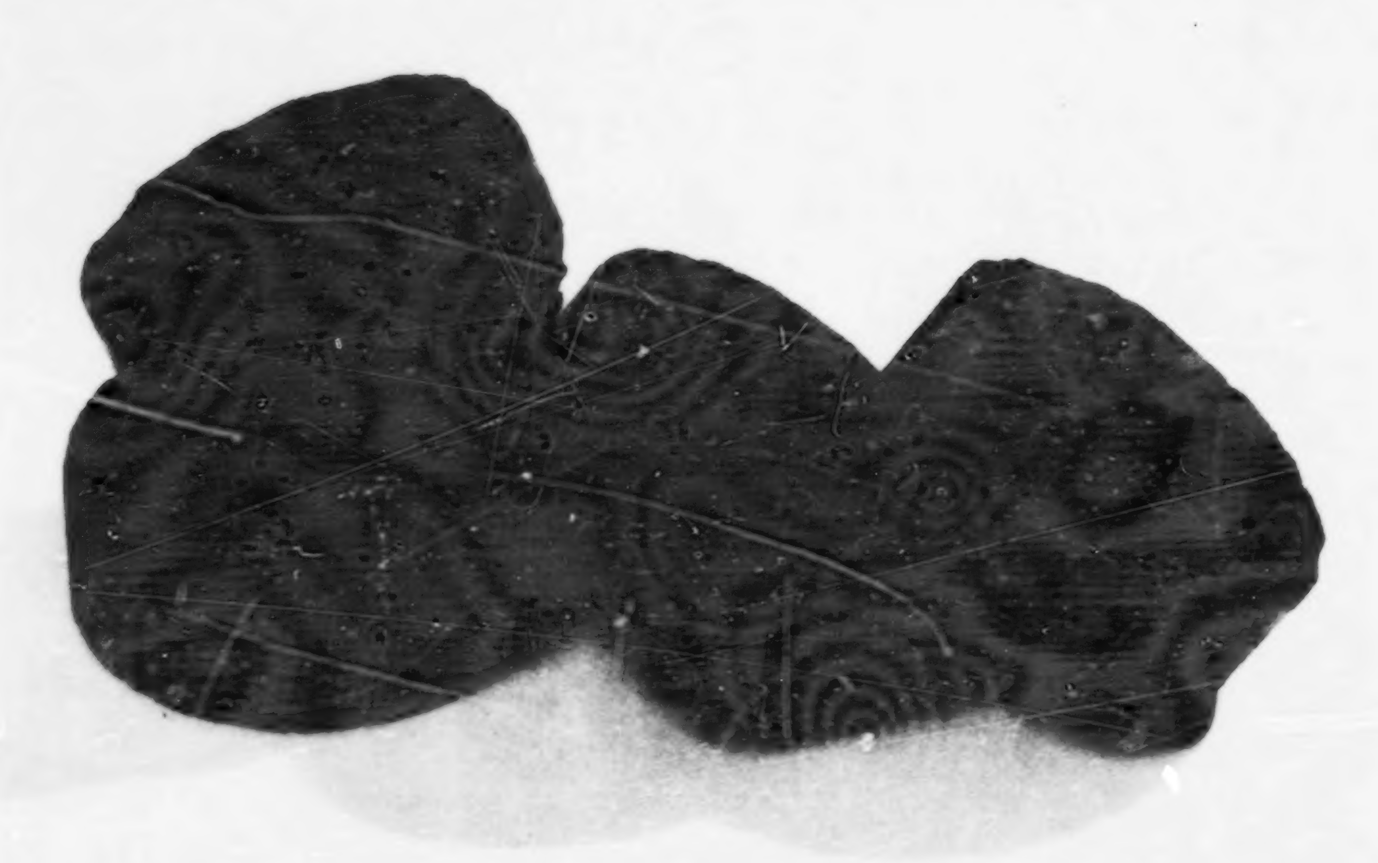

RUN OF MINE
CRUSH/SCREEN
ROCK
COAL
GRAVI-
SEPARATOR
1.3 SP. GR.
LEACH
SOLUTION
FLOAT
SINK
FILTER/ WASH
MEYERS PROCESS
0.8#
+
1.2 - 1.5#
$S_x$
$CaSO_4$

Figure 23. Gravichem Process



MEYERS PROCESSED COAL WHICH HAS BEEN BRIQUETTED WITHOUT BINDER

Figure 24. Hot-Briquetted Coal (1" -Size)

## TABLE 18. EQUILIBRIUM GRAVICHEM TESTS ON 14 MESH x 0 MARTINKA MINE COAL WITH VARIATION OF MEDIUM AND SEPARATION TIME

| | | | Fraction, % w/w of Coal*** | | Total Sulfur, % w/w | | | Heat Content, Btu/lb | | | Sulfur Content, lbs S/$10^6$ Btu | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sp Gr | Separation Time, hrs | Float | Sink | Float | Sink | Processed Sink+ | Float | Sink | Processed Sink+ | Float | Sink | Processed Sink+ |
| 1. | 1.30* | 0.25 | 27.6 | 72.4 | 0.75 | 1.89 | -- | 14711 | 12041 | -- | 0.51 | 1.57 | -- |
| 2. | 1.28** | 3 | 23.0 | 77.0 | 0.80 | 1.45 | 0.79 | 15057 | 12917 | 13105 | 0.53 | 1.12 | 0.60 |
| 3. | 1.28** | 16 | 31.0 | 69.0 | 0.72 | 1.39 | 0.86 | 14628 | 12810 | 12907 | 0.49 | 1.09 | 0.67 |
| 4. | 1.28** | 46 | 24.0 | 76.0 | 0.69 | -- | -- | 14829 | -- | -- | 0.47 | -- | -- |
| 5. | 1.33** | 3 | 33.0 | 67.0 | 0.77 | 1.56 | -- | 14604 | 12665 | -- | 0.53 | 1.23 | -- |
| 6. | 1.33** | 16 | 40.0 | 60.0 | 0.76 | 1.56 | -- | 14748 | 12435 | -- | 0.52 | 1.25 | -- |
| 7. | 1.43** | 3 | 48.0 | 52.0 | 0.83 | 2.11 | -- | 14336 | 12108 | -- | 0.58 | 1.74 | -- |
| | | | | | 0.80 | 2.26 | -- | 14413 | 11956 | -- | 0.56 | 1.89 | -- |

*Mixture of toluene and perchloroethylene, wt ratio 1:1.35.

**Aqueous ferric sulfate at 80°C with specific gravity obtained as follows:

| | $Fe^{+++}$ as $Fe_2(SO_4)_3$ (wt %) | $H_2SO_4$ (wt %) | $H_2O$ (wt %) |
|---|---|---|---|
| 1.28 = | 7.5 | 4 | 88.5 |
| 1.33 = | 5.0 | 21 | 74 |
| 1.43 = | 5.0 | 30 | 65 |

+Heated at 100°C for 24 hrs in aqueous ferric sulfate separation media, washed with water, then extracted with toluene and dried.

***Filtered from separation medium, washed of leached solution treated and dried to constant weight in a vacuum oven at 100°C.

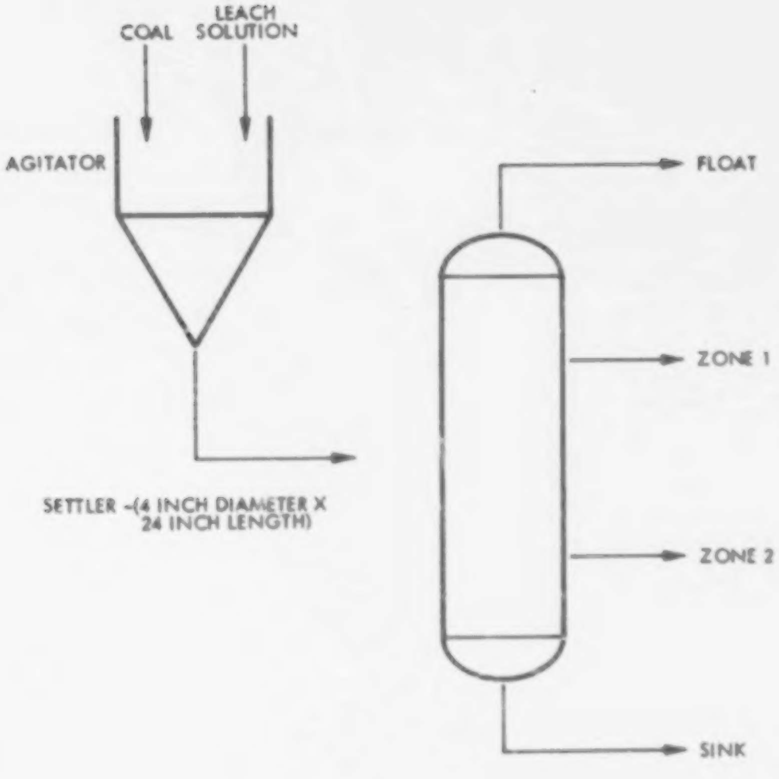

COAL
LEACH SOLUTION
AGITATOR
SETTLER -(4 INCH DIAMETER X 24 INCH LENGTH)
FLOAT
ZONE 1
ZONE 2
SINK

Figure 25. Bench-Scale Gravichem Test Apparatus Flow Diagram

equivalent to that obtained with organic solvents of the same density. However, the sulfur content of the Gravichem float products, at 1.28 specific gravity, decreases with increasing time of gravity separation (Experiments 2-4) indicating that leaching of pyritic sulfur is taking place, as expected, during the gravity separation. Similarly, the sink fraction is undergoing significant pyrite leaching — e.g., a sulfur content of 1.89% w/w is seen for the sink coal obtained from organic solvent but a sulfur content of 1.39-1.45% w/w is seen for the Gravichem sink. The Gravichem sink material has greatly enhanced heat content relative to the organic solvent sink coal because of dissolution of coal mineral matter in addition to pyrite (Experiments 2-6).

Increasing the specific gravity of the iron sulfate leach solution gives increased yields of float coal with only slightly higher sulfur content and slightly less heat content (Experiments 5-7). No definite trend is seen for the relative amounts of float material as separation is varied from 3 to 46 hours (Experiments 2-4), while a possible trend is seen at 1.33 specific gravity between 3 hours and 16 hours.

Coal from the Kentucky No. 9 Mine, supplied by the TVA Cumberland Power Plant, was likewise processed by the Gravichem method. Ground coal at 3/8-inch topsize was mixed with iron sulfate leach solutions of 1.28-1.34 specific gravity (Figure 26), heated to 80°C and allowed to gravity separate in a holding tank to give a 38-52% w/w yield of float product, after removal of residual iron sulfate leach solution. The float product (Table 19) from all of the separations is a power plant fuel containing 3.09-3.50 lbs $SO_2/10^6$ Btu, having a heat content range between 13774 and 14354 Btu/lb. The sink fractions (48-62% w/w) contain most of the coal pyrite.

The sink coal was size-reduced while still in leach solution to a 14 mesh x 0 coal/leach solution slurry (Table 20), then treated at 102°C according to Meyers Process procedures. The product contained less than 4 lbs $SO_2/10^6$ Btu. Thus, both float and processed sink coals meet the Tennessee State Implementation Standard requirements of 4 lbs $SO_2/10^6$ Btu. A substantial decrease in coal pyrite actually has occurred.

Gravity separation and chemical processing of Kentucky Mine No. 9 coal produced a significant reduction in ash and total sulfur and an increase in heat content as noted in Table 19. A more extensive analysis summary is

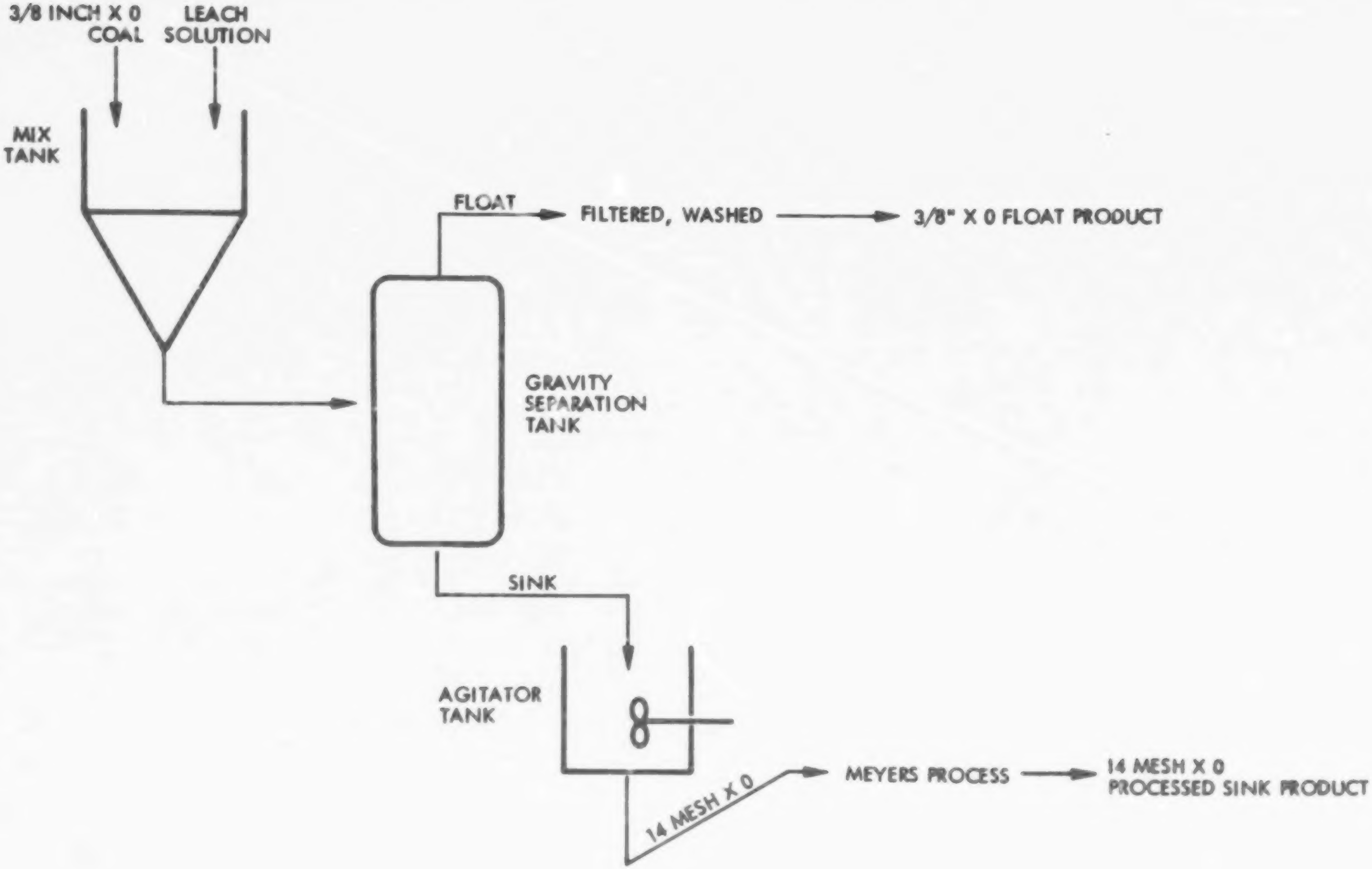

3/8 INCH X 0 COAL
LEACH SOLUTION
MIX TANK
FLOAT
FILTERED, WASHED
3/8" X 0 FLOAT PRODUCT
GRAVITY SEPARATION TANK
SINK
AGITATOR TANK
14 MESH X 0
MEYERS PROCESS
14 MESH X 0 PROCESSED SINK PRODUCT

Figure 26. Gravichem Processing of TVA Coal

## TABLE 19. EQUILIBRIUM GRAVICHEM TESTS AT 80°C ON 3/8" TOP-SIZE KENTUCKY NO. 9 MINE COAL WITH VARIATION OF MEDIUM

| Sample | | Total Sulfur $S_T$ | Pyritic Sulfur $S_p$ | Ash % w/w | Heat Content Btu/lb. | Sulfur Content lbs $SO_2$/ $10^6$ Btu |
|---|---|---|---|---|---|---|
| As Received | #1 | 4.40 | 2.13 | 12.79 | 12408 | 7.09 |
| | #2 | 4.49 | 1.81 | 12.79 | 12414 | 7.24 |
| | #3 | 3.99 | 1.93 | 10.78 | 12687 | 6.29 |

| Exp No. | Sp. Gr. | Separation Time, hrs. | Fraction, % w/w of Coal[***] | | Total Sulfur, % w/w | | | Heat Content, Btu/lb | | | Ash, % w/w | | | Sulfur Content, lbs $SO_2/10^6$ Btu | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Float | Sink | Float | Sink | Processed Sink[+] | Float | Sink | Processed Sink[+] | Float | Sink | Processed Sink[+] | Float | Sink | Processed Sink[+] |
| 1 | 1.30[*] | 0.5 | 40 | 60 | 2.40 | 5.61 | ---- | 13889 | 11369 | ---- | 3.93 | 17.50 | ---- | 3.46 | 9.87 | ---- |
| 2 | 1.28[*] | 0.5 | 35 | 65 | 2.33 | ---- | 2.42 | 14128 | ---- | 12827 | 3 48 | ---- | 9.51 | 3.30 | ---- | 3.77 |
| 3 | 1.28[**] | 3.0 | 38 | 62 | 2.22 | 4.92 | ---- | 14354 | 12295 | ---- | 3.19 | 14.83 | ---- | 3.09 | 8.00 | ---- |
| 4 | 1.28[**] | 3.0 | 41 | 59 | 2.41<br>(2.29)[#] | 4.78 | (2.54) | 14046<br>(14322)[#] | 12004 | ---- | 3.22<br>(2.43)[#] | 14.78 | ---- | 3.30<br>(3.20)[#] | 7.96 | ---- |
| 5 | 1.30-1.34 | 3.0 | 46 | 54 | 2.27 | ---- | 2.57 | 13774 | ---- | 12973 | 3.38 | ---- | 10.40 | 3.30 | ---- | 3.96 |
| 6 | 1.30-1.34 | 3.0 | 48 | 52 | 2.35 | ---- | ---- | 14205 | ---- | ---- | 3.52 | ---- | ---- | 3.31 | ---- | ---- |
| 7 | 1.30-1.34 | 3.0 | 52 | 48 | 2.44 | ---- | 2.51 | 13960 | ---- | 12335 | 4.13 | ---- | 13.04 | 3.50 | ---- | 4.0 |

[*] Mixture of toluene and perchloroethylene, wt ratio 1:1.35.

[**] Aqueous ferric sulfate at 80°C with specific gravity obtained as follows:

| $Fe^{+++}$ as $Fe_2(SO_4)_3$ (wt %) | $H_2SO_4$ (wt %) | $H_2O$ (wt %) |
|---|---|---|
| ~ 7.5 | 4 | 88.5 |

[***] Filtered from separation medium, washed if leached solution treated and dried to constant weight in a vacuum over at 100°C.

[+] Processed in 1.3 S.G. leach solution (above) for 48 hours at 102°C subsequent to size reduction in Waring blender for 5 minutes @ 15,000 rpm.

[#] Processed float.

TABLE 20. PARTICLE SIZE DISTRIBUTION OF SIZE-REDUCED KENTUCKY NO. 9* SINK COAL

| Screen Size | Retained, % w/w |
|---|---|
| 14 | 1.75 |
| 35 | 3.73 |
| 48 | 9.25 |
| 100 | 23.72 |
| 150 | 14.10 |
| 200 | 12.92 |
| Pan | 34.32 |

[*] 3/8 inch x 0 sink coal in Gravichem leach solution, size-reduced in a Waring blender for 5 minutes at 15,000 rpm.

presented in Table 21 which, in addition to the above noted parameters, also contains sulfur forms analyses, including elemental sulfur ($S_n$) on three float samples and four processed sink fractions.

Referring to Table 21 the reduction in total sulfur is related to both pyritic and sulfate sulfur removal during gravity separation, as was noted for the Martinka coal (above), e.g., compare Experiment 3 with the organic sink in Experiment 1. Additionally, it is seen that elemental sulfur is formed during the separation process. In Experiment 3, correcting for approximately 0.10% w/w elemental sulfur* on the starting coal (Section 7.3.3) due to weathering, the amount of $S_n$ formed is greater than would be expected (0.40% w/w $\Delta S_p$) based on the amount of pyrite ($S_p$) removed. $S_n$ formed in Experiments 4 and 5 is as expected. For $\Delta S_p$ of 2.38 and 2.32% w/w during Gravichem processing, 0.95 and 0.93% w/w $S_n$ should be produced. Based on the two analyses (1.0% w/w) and correcting for 0.1% w/w $S_n$ on the starting coal, it is seen that these data are

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[*] Assumption is that sink fraction contents the majority of the elemental sulfur formed during weathering.

TABLE 21. GRAVICHEM PROCESSED KENTUCKY MINE NO. 9 COAL

| Exp No. | Coal | Gravity Fraction % | Ash % w/w | Heat Content, Btu/lb | Total Sulfur, % w/w | Pyritic Sulfur, % w/w | Sulfate Sulfur, % w/w | Organic Sulfur, % w/w | Elemental+ Sulfur, % w/w |
|---|---|---|---|---|---|---|---|---|---|
| Control Sample (As Received) | Total coal | 100 | 12.12<br>±1.16 | 12503<br>± 159 | 4.27<br>±0.22 | 1.96<br>±0.13 | 0.38<br>±0.15 | 1.92<br>±0.20 | |
| 1* | Organic Float** | 40 | 3.93 | 13889 | 2.40 | 0.54 | 0.18 | 1.68 | |
| | Organic Sink** | 60 | 17.50 | 11369 | 5.61 | 2.59 | 0.92 | 2.10 | |
| 2 | Organic Float** | 35 | 3.48 | 14128 | 2.33 | 0.33 | 0.02 | 1.98 | .03 |
| | Organic Sink*** | 65 | 9.51 | 12827 | 2.42 | 0.11 | 0.33 | 1.98 | |
| 3 | Gravichem Float** | 38 | 3.19 | 14354 | 2.22 | 0.39 | 0.01 | 1.82 | .02 |
| | Gravichem Sink** | 62 | 14.83 | 12295 | 4.92 | 2.30 | 0.10 | 2.52 | .35 |
| 4 | Gravichem Float** | 41 | 3.22 | 14046 | 2.41 | 0.38 | 0.05 | 1.98 | |
| | Gravichem Float*** | 41 | 2.43 | 14322 | 2.29 | 0.12 | 0.20 | 1.96 | |
| | Gravichem Sink** | 59 | 14.78 | 12004 | 4.92 | 2.45 | 0.26 | 2.21 | |
| | Gravichem Sink*** | 59 | --- | --- | 2.54 | 0.21 | 0.37 | 1.97 | 1.0 |
| 5 | Gravichem Float** | 46 | 3.38 | 13774 | 2.27 | 0.52 | 0.06 | 1.69 | |
| | Gravichem Sink*** | 54 | 10.40 | 12973 | 2.57 | 0.27 | 0.41 | 1.89 | 1.0 |
| 6 | Gravichem Float** | 48 | 3.52 | 14205 | 2.35 | 0.35 | 0.01 | 1.99 | |
| | Gravichem Sink*** | 52 | 11.11 | 12627 | 2.73 | 0.48 | 0.39 | 1.86 | |
| 7 | Gravichem Float** | 52 | 4.13 | 13960 | 2.44 | 0.50 | 0.04 | 1.91 | 0.05 |
| | Gravichem Sink** | 48 | 16.20 | 11767 | 4.99 | 2.20 | 0.34 | 2.45 | |
| | Gravichem Sink*** | 48 | 13.04 | 12335 | 2.51 | 0.33 | 0.31 | 1.89 | 1.40 |

* Refer to Table 5-3.

** Gravity Separation only.

*** Gravichem processed.

+ Elemental sulfur removed with toluene before coal analysis in agreement with postulated Meyers Process chemistry. Experiment 7, however, indicates a much higher formation of $S_n$ (1.30% w/w)* than would be expected from the $\Delta S_p$ (2.26% w/w), i.e., 0.90% w/w $S_n$ would be expected based on 0.4% w/w $\Delta S_p$.

With respect to the formation of $S_n$ during oxidation of pyrite by ferric ion, Yurovskii reports that it is only formed at low $Fe_2(SO_4)_3$ concentrations. Many of his experiments were conducted using 16% $Fe_2(SO_4)_3$ or 4.48% $Fe^{+++}$, which he considered high, and the presence of $S_n$ was not confirmed. The experiments on Kentucky Mine No. 9 coal, shown in Table 21 were conducted in leach solution containing 7.5% $Fe^{+++}$. Thus, Yurovskii's error in not observing $S_n$ leads to an erroneous conclusion with respect to the efficiency of $Fe_2(SO_4)_3$ as an oxidizing agent for removal of pyrite from coal. He based his conclusions for determining the degree of pyritic sulfur reduction on total sulfur (Eschka method) difference before and after processing.

Therefore the elemental sulfur, which was undoubtedly formed, increased the total sulfur of the coal and was assumed to be unreacted pyrite, thus lowering the observed efficiency of the reaction. Table 22 is a summary of Yurovskii's work on three coals of varying sulfur ash content. Also shown in the Table are data obtained on Kentucky Mine No. 9 coal for various reaction times at 102°C. Referring to Table 22, the degree of oxidation of coal pyrite ($FeS_2$), as reported by Yurovskii, based on total sulfur reduction, has been corrected for $S_n$, i.e., the theoretical amount of $S_n$ formed (0.4% w/w $\Delta S_p$) has also been converted to pyrite loss and reported in the table as corrected data. Corrections were made as follows:

$$\text{Yurovskii assumed } S_{t_i} - S_{t_f} = \Delta S_p$$

where

$S_{t_i}$ = original coal total sulfur, %,
$S_{t_f}$ = treated coal total sulfur, %,
$\Delta S_p$ = pyritic sulfur reduction, %,

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*Corrected for initial sulfur on coal.

## TABLE 22. SULFUR REMOVAL FROM COAL WITH FERRIC SULFATE SOLUTIONS

| Coal | Ash Content of Coal % w/w | Treatment | | Solution Fe Content % | Sulfur Content of Coal, % w/w | | | | Degree of Oxidation of Coal $FeS_2$, % w/w | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Original | | Treated | | | | |
| | | Time hrs. | Temp °C | | Total S | Pyritic S | Total S | Pyritic S | Yurovskii * | Corrected ** | Meyers † |
| Lutuginugol | 14.0 | 1 | 80 | 4.5 | 4.47 | 2.97 | 4.03 | 2.53 | 15 | 25 | |
| | | 1 | 90 | 4.5 | 4.47 | 2.97 | 3.70 | 2.20 | 26 | 43 | |
| | | 1 | 100 | 4.5 | 4.47 | 2.97 | 3.61 | 2.11 | 29 | 48 | |
| | | 2 | 100 | 4.5 | 4.47 | 2.97 | 3.45 | 1.96 | 34 | 57 | |
| | 7.1 | 2 | 100 | 4.5 | 5.11 | 3.38 | 3.80 | 2.07 | 40 | 67 | |
| Gorlovskugol | 8.3 | 2 | 100 | 4.5 | 3.60 | 2.34 | 2.68 | 1.33 | 43 | 72 | |
| | 4.2 | 2 | 100 | 4.5 | 4.23 | 2.74 | 2.73 | 1.24 | 54 | 90 | |
| Krasnodonugol | 21.0 | 2 | 100 | 4.5 | 4.20 | 2.72 | 3.90 | 2.42 | 11 | 18 | |
| | 9.0 | 2 | 100 | 4.5 | 5.10 | 3.37 | 3.80 | 2.07 | 40 | 67 | |
| Kentucky No. 9 (1.3 sink) | 15.5 | 2 | 102 | 7.5 | 4.92 | 2.45 | 3.16 | 1.28 | | | 48 |
| | | 4 | 102 | 7.5 | 4.92 | 2.45 | 2.91 | 1.01 | | | 59 |
| | | 8 | 102 | 7.5 | 4.92 | 2.45 | 2.65 | 0.62 | | | 75 |
| | | 14 | 102 | 7.5 | 4.92 | 2.45 | 2.43 | 0.37 | | | 85 |
| | | 32 | 102 | 7.5 | 4.92 | 2.45 | 2.45 | 0.25 | | | 90 |
| | | 48 | 102 | 7.5 | 4.92 | 2.45 | 2.54 | 0.21 | | | 91 |

* Yurovskii's data as presented.

** Yurovskii's data corrected for elemental sulfur.

† Experimental Meyers Process.

However, from theory (above) $S_{t_i} - (S_{t_f} - S_n) = \Delta S_p$ (Assume $S_n = 0.4\ \Delta S_p$)

$$S_{t_i} - S_{t_f} = \Delta S_p - 0.4\ \Delta S_p$$

$$\Delta S_p = \frac{S_{t_i} - S_{t_f}}{0.6}$$

$$\text{Degree of oxidation, \%} = \frac{\Delta S_p}{\text{Original Pyritic S, \%}}$$

It is also seen in Table 22 that Kentucky Mine No. 9 sink coal has a comparable, although lower, degree of oxidation of coal pyrite (compare with 2 hours @ 100°C - Lutuginugol, 14% ash). Comparing the reaction rate constant ($K_L$) in Figure 27 of Kentucky Mine No. 9 coal ($K_L$ = 0.14 hours$^{-1}$ $W_p^{-1}$) with Yurovskii's Lutuginugol coal (0.21 hours $^{-1}$ $W_p^{-1}$), it is seen that the pyrite oxidation rate is 67% of the Lutuginugol coal $K_L$. Y = 0.96 was estimated for Yurovskii's work since he used 12 grams of coal in 100 ml of 16% $Fe_2(SO_4)_3$ leach solution.

The effect of ash content on coal pyrite oxidation rate was noted by Yurovskii. Plotting the corrected data from Table 22 (2 hours @ 100°C) for each coal (degree of oxidation versus ash content), it is seen in Figure 28 that a correlation does exist. It may be noted that Kentucky Mine No. 9 coal supports the correlation. Based on these data, the $K_L$ for Kentucky Mine No. 9 coal (15.5% ash) should be lower than 14% Lutuginugol, although not as low as was observed.

A final comparison of the work of Yurovskii and data obtained on Kentucky Mine No. 9 coal is seen in Table 23. As was noted earlier for Kentucky Mine No. 9 coal, Yurovskii also observed a large reduction in ash content of the coal fraction separated by his chemicogravitational process. It may be noted that a comparable degree of cleaning is noted for the two methods although Kentucky No. 9 was cleaned at a larger particle size (0-9 mm).

### 7.2.3 Non-Equilibrium Separation

Following the equilibrium Gravichem separation studies (Section 7.2.2) it was desirable to investigate non-equilibrium Gravichem float-sink separation which would more nearly be the case in a process plant.

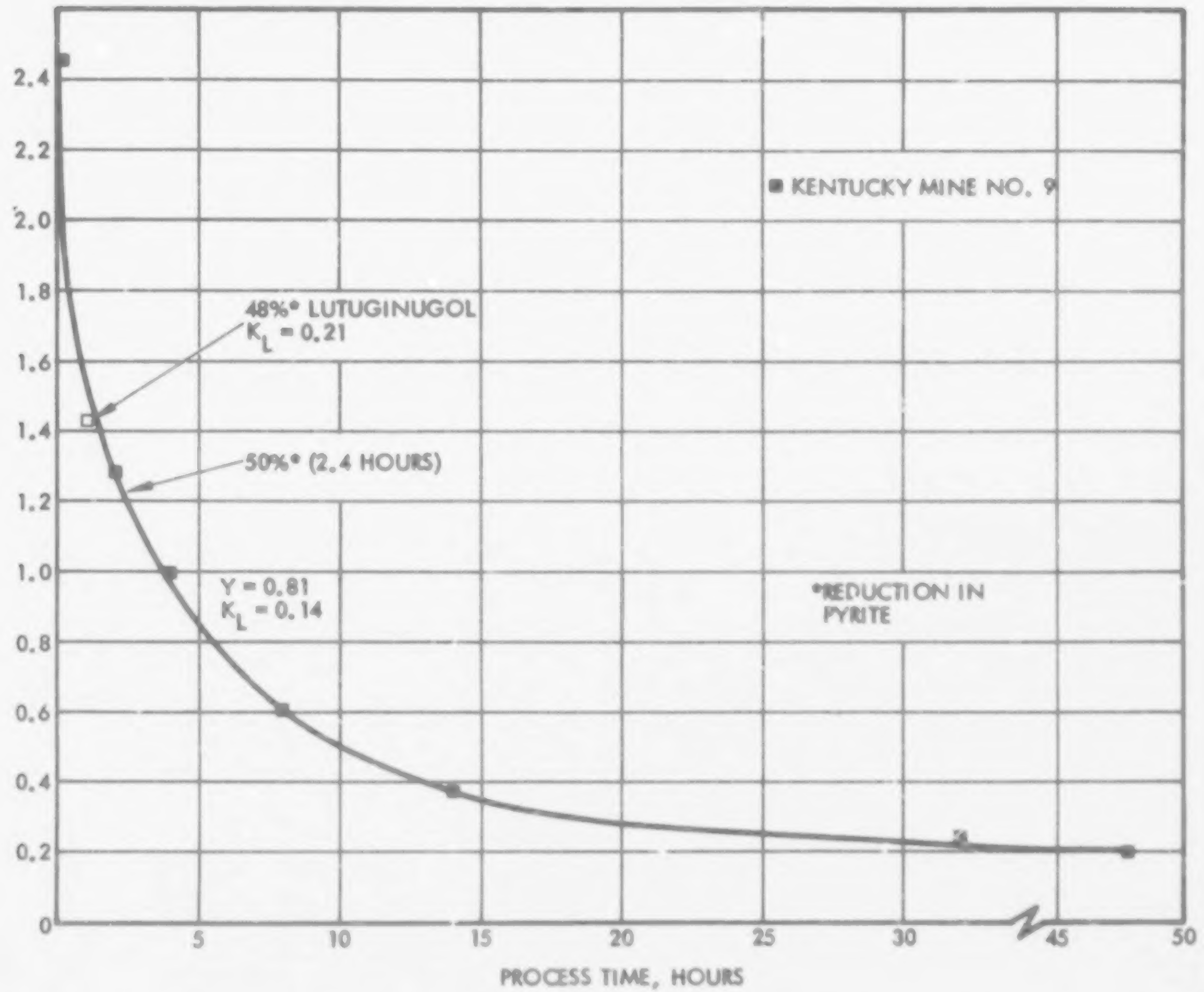

Figure 27. Puritic Sulfur Leaching Data for 1.3 Specific Gravity Sink Coal at 102°C (Kentucky Mine No. 9)

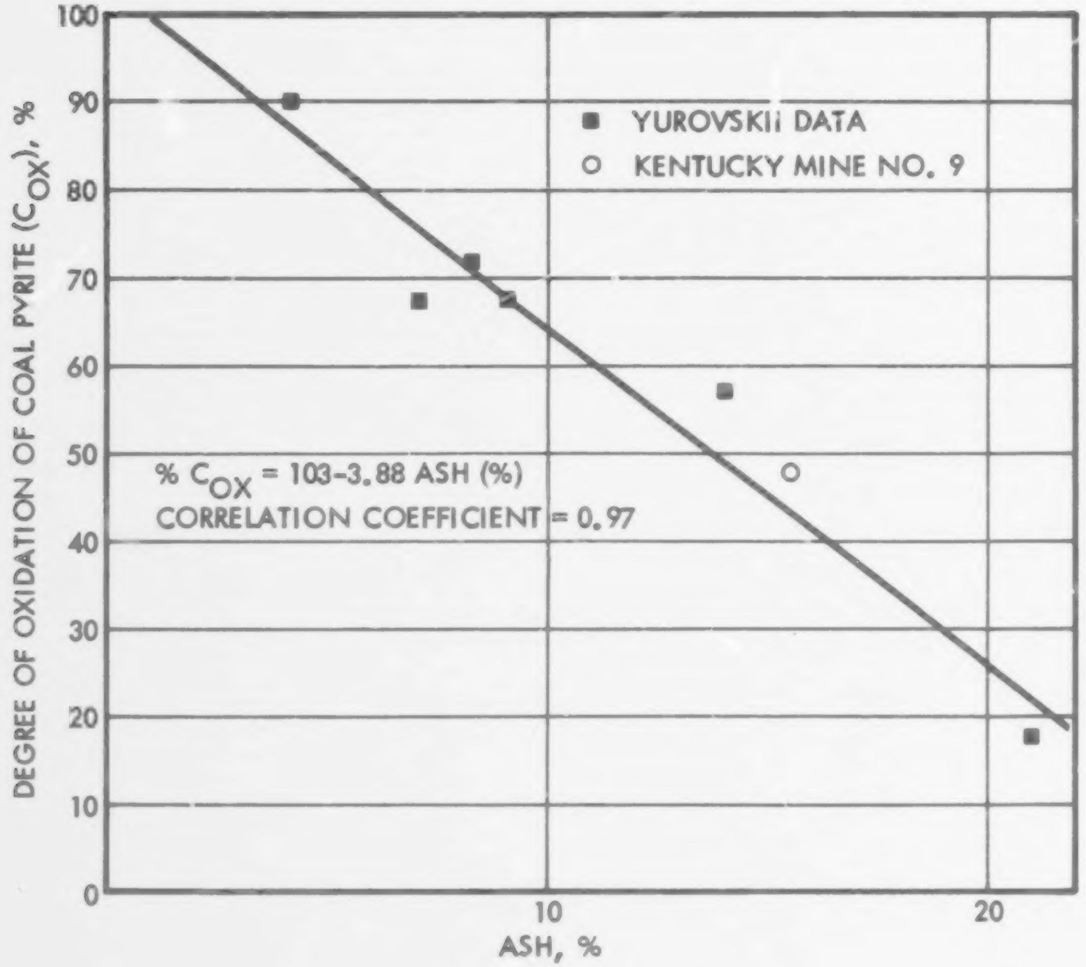

Figure 28. Coal Oxidation After Two Hours at 100°C as a Function of Ash Content

TABLE 23. COMPARATIVE RESULTS OF CLEANING

| Method | Coal Size, mm | Original Coal, % w/w |  | Float, % w/w |  |  |
|---|---|---|---|---|---|---|
|  |  | Ash | Total Sulfur | Yield | Ash | Sulfur |
| Chemicogravitational (Yurovskii) | 0-3 | 25.79 | 5.82 | 60 | 4.50 | 2.17 |
| Gravichem (Kentucky No. 9) | 0-9 | 12.12 | 4.27 | 52 | 4.13 | 2.44 |
|  |  | 12.12 | 4.27 | 48 | 3.52 | 2.35 |
|  |  | 12.12 | 4.27 | 46 | 3.38 | 2.27 |

Sampling ports were added to the bench scale Gravichem separator (Figure 25) and the float fraction was skimmed off the top of the leach solution as before, while coal particles and leach solution in zones 1 and 2 were removed through valves and finally the sink fraction was obtained by separating from the filtrate. This allows isolation of coal "in transit" for a first preliminary look at the behavior of float and sink particles in a dynamic situation.

Two series of non-equilibrium Gravichem float/sink separations were conducted with Martinka coal at 80$^{o}$C using 1.2 and 1.3 specific gravity (S.G.) leach solutions. Other experimental parameters include:

- Weight of coal: 900 g (nominal).
- Weight of leach solution: 3600 g (nominal).
- Coal size: 14 mesh.

The results for 1.3 S.G. leach solution (Table 24) show that the samples taken were indeed non-equilibrium, in that times greater than 2 hours would be required for the slurry to have attained equilibrium.

It may be noted that the combined float and zone 1 fractions (1.3 S.G.) are representative of the float portion taken in equilibrium Gravichem separation (Btu, ash, total sulfur, pyritic sulfur, etc.) as shown in Table 18. Likewise, the combined zone 2 and sink portions are comparable to equilibrium sink percent recovery (coal % w/w) in Table 18; however, the zone 2 fraction in Table 24 is more nearly like the combined float and zone 1 fractions in the same study. Thus, non-equilibrium Gravichem shows a greater yield of clean

## TABLE 24. ANALYSES OF FRACTIONS OF MARTINKA COAL OBTAINED FROM NONEQUILIBRIUM FLOAT/SINK EXPERIMENTS

| Fraction | Time Hrs. | S.G. of Leach Solution | Coal % w/w | Sulfur Analysis - % w/w | | | | Heat Content Btu/lb. | Ash % w/w | Sulfur Content - lbs S/$10^6$ Btu | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $S_t$ | $S_p$ | $S_s$ | $S_o$ | | | Individual Fraction | FL+Z1** | FL+Z1+Z2** |
| Float | 0.5 | 1.3 | 10.0 | 0.79 | 0.13 | Tr* | 0.65 | 14851 | 4.22 | 0.53 | | |
| | 1.0 | 1.3 | 14.0 | 0.87 | 0.13 | Tr | 0.73 | 14650 | 5.35 | 0.59 | | |
| | 2.0 | 1.3 | 14.0 | 1.01 | 0.18 | Tr | 0.82 | 14454 | 6.25 | 0.70 | | |
| Zone 1 | 0.5 | 1.3 | 21.3 | 0.91 | 0.16 | Tr | 0.74 | 14604 | 6.39 | 0.62 | 0.59 | |
| | 1.0 | 1.3 | 21.0 | 0.79 | 0.12 | Tr | 0.66 | 14642 | 5.41 | 0.54 | 0.56 | |
| | 2.0 | 1.3 | 23.9 | 0.81 | 0.14 | Tr | 0.66 | 14635 | 5.31 | 0.55 | 0.61 | |
| Zone 2 | 0.5 | 1.3 | 30.3 | 0.96 | 0.26 | Tr | 0.69 | 14069 | 8.46 | 0.68 | | 0.63 |
| | 1.0 | 1.3 | 23.0 | 0.92 | 0.27 | Tr | 0.65 | 14105 | 8.27 | 0.65 | | 0.60 |
| | 2.0 | 1.3 | 17.0 | 0.84 | 0.16 | Tr | 0.67 | 14136 | 7.84 | 0.59 | | 0.60 |
| Sink | 0.5 | 1.3 | 38.4 | 1.76 | 1.15 | Tr | 0.60 | 11357 | 23.95 | 1.55 | | |
| | 1.0 | 1.3 | 42.0 | 1.72 | 0.98 | Tr | 0.73 | 11132 | 23.85 | 1.55 | | |
| | 2.0 | 1.3 | 46.0 | 1.66 | 0.92 | Tr | 0.73 | 11732 | 21.87 | 1.41 | | |
| Total Coal (Weighted Average) | 0.5 | 1.3 | | 1.24 | 0.57 | Tr | 0.66 | 13220 | 13.54 | 0.94 | | |
| | 1.0 | 1.3 | | 1.24 | 0.54 | Tr | 0.69 | 12951 | 14.30 | 0.96 | | |
| | 2.0 | 1.3 | | 1.24 | 0.51 | Tr | 0.72 | 13321 | 13.54 | 0.93 | | |
| Starting Coal | --- | --- | --- | 1.61 | 0.72 | 0.18 | 0.71 | 12950 | 14.70 | 1.24 | | |

* Trace; values for $S_s$ were $\leq 0.01$; 0.01 was used for $S_o$ calculation (starting coal excepted).

** Weighted average of Float (FL) and Zone 1 (Z1) or Float and Zone 1 and Zone 2 (Z2).

coal may be attained at 1.3 S.G. than was noted in the preceding equilibrium studies (Section 7.2.2).

Table 25 includes the non-equilibrium data obtained at 1.2 S.G. Forty-three percent of the coal is retained in zone 1 and zone 2 at 0.2 hours, which has Btu, ash and total sulfur content comparable to zone 1 and zone 2 fractions obtained at 1.3 S.G. after 0.5 hours. The recovered coal, however, is less for the 1.2 S.G. separation (43% versus 52%), plus an additional 10% of float was also recovered from the 1.3 S.G. 0.5 hours separation. With respect to the 1.2 S.G. separation, although more coal was recovered in zone 1 and zone 2 (51%) for 0.1 hours at 1.2 S.G. than for 0.2 hours (43%), the total sulfur and heat content, however, indicate a less-clean coal fraction compared to the 0.2 hours 1.2 S.G. (0.70 and 0.63 lbs S/$10^6$ Btu, respectively).

Particle size distributions for each coal density fraction listed in Table 24 are shown in Figure 29. It is seen that although the percentage distribution of particles is comparable between 1 and 2 hours for each mean particle size (mesh) within the float and zone 1 and 2 fractions, the decrease in 60 mesh and increase in pan (-200 mesh), within the sink fraction, suggests that equilibrium has not been achieved.

Based on the work of Yurovskii (op cit) and the application of Stokes Law, it is not to be expected that small particles will attain equilibrium within the system due to gravity alone over short periods of time. It is well known that the velocity at which fine particles settle in heavy liquids is given by Stokes Law:

$$V = \frac{2}{9}\frac{r^2}{n}(\rho_2 - \rho_1)\,g$$

where

$r$ = mean particle radius, cm,
$\rho_1$ = density of the liquid, g/cc
$\rho_2$ = density of the settling particle, g/cc,
$n$ = viscosity of liquid, poise, and
$g$ = acceleration due to gravity.

## TABLE 25. ANALYSES OF FRACTIONS OF MARTINKA COAL OBTAINED FROM NONEQUILIBRIUM FLOAT/SINK EXPERIMENTS

| Fraction | Time Hrs. | S.G. of Leach Solution | Coal % w/w | Sulfur Analysis - % w/w | | | | Heat Content Btu/lb. | Ash % w/w | Sulfur Content - lbs S/$10^6$ Btu | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $S_t$ | $S_p$ | $S_s$ | $S_o$ | | | Individual Fraction | FL+Z1*** | FL+Z1+Z2*** |
| Float | 0.2 | 1.2 | 0.2 | ** | | Tr* | | | | | | |
| Zone 1 | 0.1 | 1.2 | 22.5 | 0.98 | 0.22 | Tr | 0.75 | 14050 | 7.97 | 0.70 | 0.70 | |
| | 0.2 | 1.2 | 14.0 | 0.90 | 0.18 | Tr | 0.71 | 14234 | 7.61 | 0.63 | 0.63 | |
| Zone 2 | 0.1 | 1.2 | 28.5 | 0.99 | 0.23 | | 0.75 | 13992 | 8.45 | 0.71 | | 0.71 |
| | 0.2 | 1.2 | 28.6 | 0.88 | 0.22 | | 0.65 | 14189 | 8.03 | 0.62 | | 0.62 |
| Sink | 0.1 | 1.2 | 49.0 | 1.55 | 0.89 | | 0.65 | 12250 | 18.83 | 1.26 | | |
| | 0.2 | 1.2 | 57.2 | 1.49 | 0.86 | | 0.62 | 12446 | 18.06 | 1.20 | | |
| Total Coal (Weighted Average) | 0.1 | 1.2 | | 1.26 | 0.55 | | 0.70 | 13151 | 13.43 | 0.95 | | |
| | 0.2 | 1.2 | | 1.23 | 0.58 | | 0.64 | 13157 | 13.67 | 0.93 | | |
| Starting Coal | --- | --- | --- | 1.61 | 0.72 | 0.18 | 0.71 | 12950 | 14.70 | 1.24 | | |

* Trace; values for $S_s$ were ≤ 0.01; 0.01 was used for $S_o$ calculation (starting coal excepted).

** Insufficient coal to process for analysis.

*** Weighted average of Float (FL) and Zone 1 (Z1) or Float and Zone 1 and Zone 2 (Z2).

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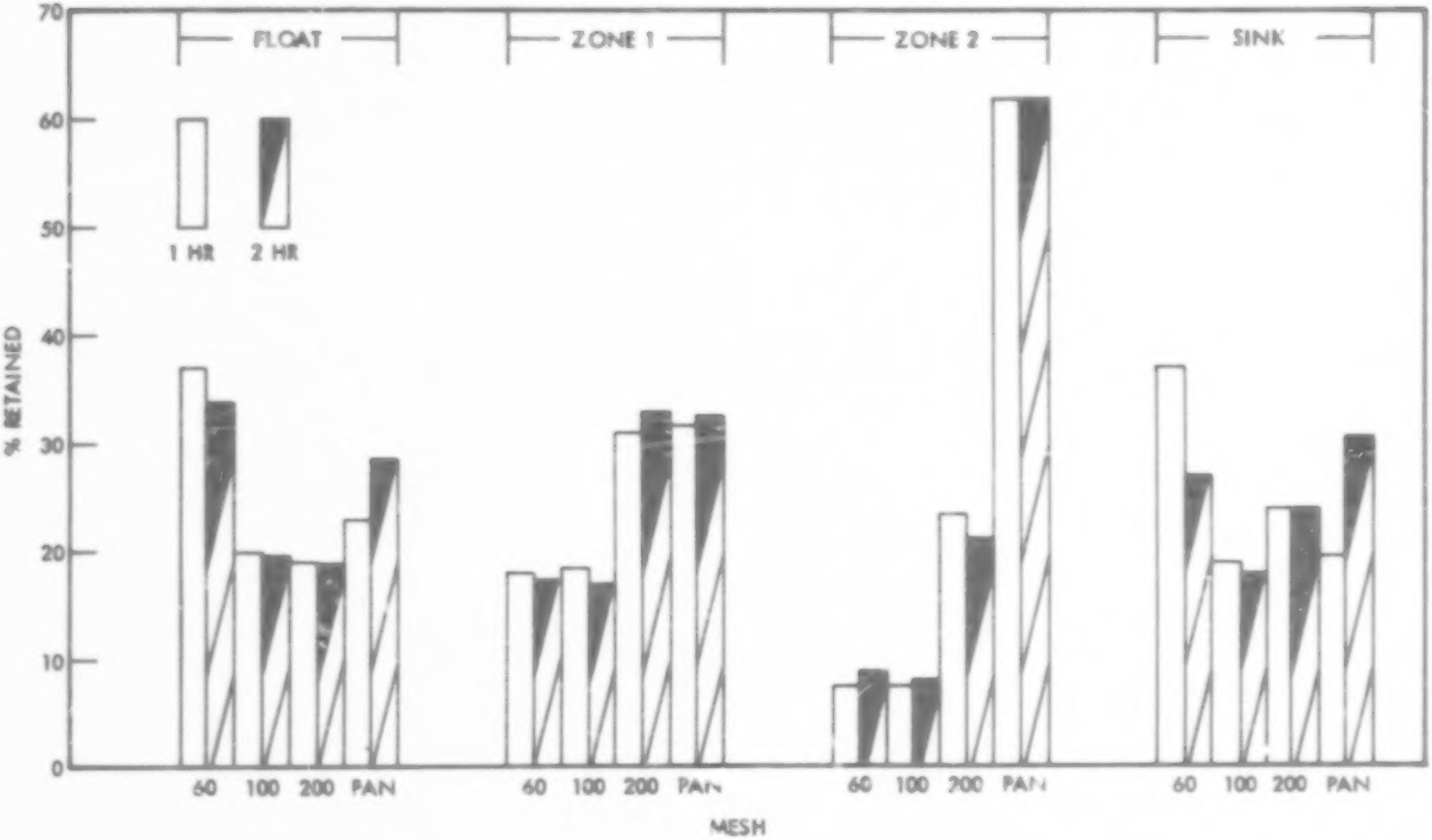

Figure 29. Particle Size Distribution in Fractions of RTU 3 Coal

It was pointed out by Yurovskii that for particles of a given diameter and specific gravity, an increase in the speed of particle movement is possible only when the speed will depend not on acceleration due to gravity, g, but on the acceleration due to centrifugal force, i.e.,

$$V_c = \frac{2}{9}\frac{r^2}{n}(\rho_2 - \rho_1)\,Cg$$

where

$$C_g = \frac{r_c n^2}{90}$$

$r_c$ = rotational radius of centrifuge, cm,

$n$ = number of revolutions of the centrifuge/min (rpm).

Table 26 illustrates the relative sensitivity of small particles of Martinka coal and pyrite to gravitational and centrifugal forces with respect to velocity of settling. It may be noted that the interaction effects (particle-particle) are not included in this comparison; thus, the velocities are in reality lower than those given.

It is seen that the centrifugal method is particularly effective and would enhance coal separation in the Gravichem process. The effectiveness of the centrifugal method is demonstrated by Yurovskii's data in Table 27, wherein he compares a flotation and centrifugal separation of a coal containing originally 24.5% w/w ash and 3.21% w/w sulfur. It is seen that for essentially equal concentrate yield from 1.5 S.G. solution, the centrifugal method gives a much cleaner concentrate (float).

It was desirable to investigate the non-equilibrium float/sink process further by assessing the effect upon coal separation (yield) when discrete particle size fractions of Martinka coal are used, i.e., the standard input coal (14 mesh x 0) used in the preceding experiments (Tables 24, 25) was separated into four particle size fractions (+60, -60 x 100, -100 x 200, -200 mesh). Non-equilibrium float sink experiments were conducted at 80°C on each of the four fractions for 30 minutes in 1.3 S.G. leach solution, as described above. It is seen in Table 28 that the combined yield for float, zone 1 and zone 2 fractions is similar to the previous experiment (Table 24) using the whole coal.

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| Particle | Particle Size (mesh) | Particle Size (cm) | Density of Particle (g/cc) | Gravitational Velocity cm/sec* | Centrifugal Velocity** (1000 rpm) cm/sec | |
|---|---|---|---|---|---|---|
| | | | | | $r_c$ = 10 | $r_c$ = 300 |
| Coal | 100 | 0.015 | 1.45 | $9 \times 10^{-3}$ | 1.02 | 30 |
| | 200 | 0.0074 | 1.45 | $2 \times 10^{-5}$ | $2 \times 10^{-3}$ | $6 \times 10^{-2}$ |
| Pyrite | 100 | 0.015 | 5.0 | 0.22 | 24.9 | 747 |
| | 200 | 0.0074 | 5.0 | $5.6 \times 10^{-4}$ | $6.3 \times 10^{-2}$ | 1.89 |

* $V = \frac{2}{9} \frac{r^2}{n} (\rho_2 - \rho_1)\, g$

** $V = \frac{2}{9} \frac{r^2}{n} (\rho_2 - \rho_1) \frac{r_c n^2}{90}$

TABLE 27. FLOTATION AND CENTRIFUGAL SEPARATION ON COALS*

| Original Coal, % w/w | | | Cleaning Method | Concentrate, % w/w | | |
|---|---|---|---|---|---|---|
| Sample Source | Ash | Sulfur | | Yield | Ash | Sulfur |
| Irminskaya TsOF | 31.0 | 5.30 | Flotation proper | 71.9 | 14.7 | 3.70 |
| | | | Cleaning flotation (with a depressor) | 62.0 | 9.9 | 3.55 |
| | | | Centrifugal separation in sulfate solution | 62.8 | 6.2 | 2.60 |
| | | | Centrifugal separation after preliminary chemical treatment | 62.4 | 3.7 | 1.84 |
| Kalmiusskaya TsOF | 24.5 | 3.21 | Flotation proper | 79.8 | 11.0 | 2.60 |
| | | | Cleaning flotation (with a depressor) | 69.5 | 8.2 | 2.61 |
| | | | Centrifugal separation in sulfate solution | 68.4 | 4.4 | 1.86 |

* Table 80, Yurovskii(12)

TABLE 28. YIELD OF MARTINKA COAL SEPARATED IN NONEQUILIBRIUM FLOAT/SINK EXPERIMENTS AFTER 0.5 HOURS @ 80°C (S.G. 1.3)

| Feed Coal Size Fraction (Mesh) | Feed Coal Weight (gm) | Recovered Coal (gm) | | | | Recovery |
|---|---|---|---|---|---|---|
| | | Float | Zone 1 | Zone 2 | Sink | % |
| -200 | 537 | 5 | 177 | 200 | 130 | 95 |
| -100 x +200 | 725 | 3 | 302 | 161 | 235 | 97 |
| - 60 x +100 | 776 | 160 | 194 | 76 | 344 | 99 |
| - 14 x +60 | 792 | 194 | 126 | 32 | 425 | 98 |
| Cumulative Fraction Recovered | | 13% | 29% | 17% | 41% | |
| Fraction Recovered from 14 x 0 mesh Coal* | | 10% | 21% | 30% | 38% | |

* 0.5 hour, 1.3 S.G. from Table 23.

Likewise, the sink fraction is comparable. It is noted, however, that the yield of zone 1 and zone 2 is approximately reversed which indicates that some lower specific gravity coal may be contained in zone 2 in the previous experiment.

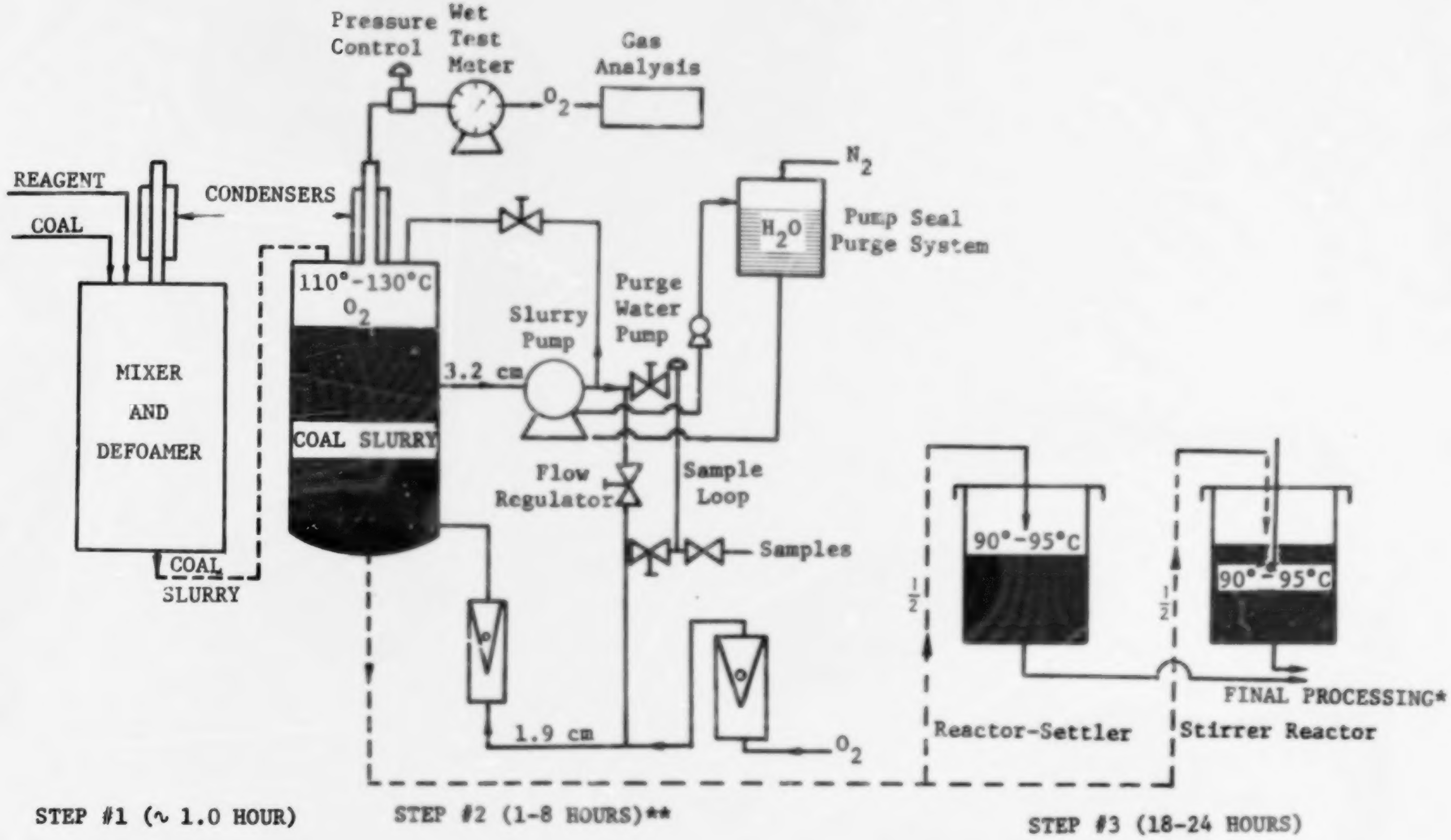
Referring again to Figures 29 and 30, one notes that the total sulfur, based on the weighted average for total coal, decreases ~0.35% w/w. This is seen at either 0.1 hours (S.G. 1.2) or 2 hours (S.G. 1.3). Such a decrease cannot be accounted for (including a correction for removal of $S_s$) on the basis of the rate constant ($K_L$) for removal of pyritic sulfur ($S_p$) from Martinka coal. However, the data show the decrease to be consistent for all of the experiments in both tables. A series of experiments were conducted at 80°C with 14 mesh Martinka coal wherein samples were wetted by 30 minutes prefoaming, leached separately in water and 4% w/w aqueous $H_2SO_4$ solution for 1 hour, and for 0.5, 1 and 3 hours in 4% w/w aqueous $H_2SO_4$ containing 7.5% iron by weight.

Subsequent coal analyses from these experiments are presented in Table 29. The following observations are made from these data.

- The leached coal total sulfur decreases primarily as a result of reductions in sulfate and organic sulfur forms.
- Since organic sulfur is not water soluble and since the organic sulfur value of the feed coal analyzed abnormally high, it can can be concluded that the reduction in total sulfur by water and by dilute $H_2SO_4$ represents sulfate leaching (the reduction in organic sulfur is attributed to errors by sulfur forms analyses).
- Elemental sulfur formed indicates a maximum of 0.12% w/w reduction in pyrite during treatment with acid-Fe reagent (assuming 0.03% present as a result of weathering).

## 7.3 PROCESSING OF RTU COAL

Experimental studies were conducted at bench-scale level to evaluate processing variables and their attendant effect on sulfur removal from Martinka mine cleaned coals in support of the RTU. A series of experiments were completed which include pressurized bench-scale processing at 120°C and 135°C, and unpressurized processing at 102°C. Additional tasks included determination of the density of leach solution/coal (slurry) and evaluation of the weathering of RTU candidate coals.


Pressure Control
Wet Test Meter
Gas Analysis
$O_2$
REAGENT
COAL
CONDENSERS
$N_2$
$H_2O$
Pump Seal Purge System
MIXER AND DEFOAMER
110°-130°C
$O_2$
COAL SLURRY
Purge Water Pump
Slurry Pump
3.2 cm
Flow Regulator
Sample Loop
Samples
COAL SLURRY
1.9 cm
$O_2$
90°-95°C
90°-95°C
1/2
1/2
FINAL PROCESSING*
Reactor-Settler
Stirrer Reactor
STEP #1 (∿ 1.0 HOUR)
STEP #2 (1-8 HOURS)**
STEP #3 (18-24 HOURS)

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* Final processing includes elemental sulfur recovery, coal washing and drying.

** Reactor volume ∿ 13 liters.

Figure 30. Bench-Scale Coal Leaching and Reagent Regeneration Apparatus

## TABLE 29. LEACHING OF MARTINKA COAL AT 80°C

| Reagent | Time Hrs. | *Coal Analyses %, w/w | | | | |
|---|---|---|---|---|---|---|
| | | Total Sulfur $S_t$ | Pyritic Sulfur $S_p$ | Sulfate Sulfur $S_s$ | Organic Sulfur $S_o$ | Elemental Sulfur $S_n$ |
| **Feed Coal** | | 1.62 | 0.72 | 0.18 | 0.72 | 0.03*** |
| Water | 1.0 | 1.35 | 0.84 | Tr** | 0.50 | 0.03 |
| 4% $H_2SO_4$ in Water | 1.0 | 1.27 | 0.76 | Tr | 0.50 | 0.04 |
| 4% $H_2SO_4$ + 7.5% Fe in $H_2O$ | 0.5 | 1.30 | 0.75 | Tr | 0.55 | 0.06 |
| | 1.0 | 1.15 | 0.68 | Tr | 0.47 | 0.06 |
| | 3.0 | 1.23 | 0.64 | Tr | 0.59 | 0.08 |

* Coal analyses performed after removal of elemental sulfur (except feed coal)

** <0.01%, reported as trace

*** Included in the organic sulfur column

### 7.3.1 Pressurized Bench-Scale Processing

Experimental studies were conducted in the pressurized bench-scale reactor (Figure 30) as described previously(5), using 14 mesh Martinka coal processed at 135°C and 100 psig $O_2$ pressure. The object of the study was to investigate the effect of reduced $Fe^{+++}$ and acid ($H_2SO_4$) concentrations on the removal of sulfur from this coal under simulated RTU conditions. It is seen in Table 30 (Experiments 1 and 2) that the amount of sulfur removal is not affected by a reduction in $Fe^{+++}$ and acid concentrations when compared to coal processed in 5% $Fe^{+++}$ and 4% $H_2SO_4$ standard RTU leach solution [Reference Experiment 01-10 (2P; 12F)].

### 7.3.2 Ambient Pressure Bench Scale Processing

Gravichem separation of coal using leach solution with various densities achieved by increasing the acid or Fe content, required the investigation of these solutions with respect to their suitability as reagents for the Meyers Process.* It was demonstrated in Section 7.2 that 7.5% $Fe^{+++}$ and 4% acid is a suitable leach solution as shown by the reduction of inorganic sulfur in Kentucky Mine No. 9 coal. It has also been shown (Table 30, Experiment 3) that high (20%) $H_2SO_4$ concentration does not change the response of inorganic sulfur to the oxidizing reaction of the Meyers Process. A significant reduction in ash and increase in heat content is noted, however, with the higher acid concentrations.

### 7.3.3 Weathering of RTU Coal

A study was conducted to determine the effect of coal particle size on weathering of Martinka coal. RTU coal No. 1 was used for these tests since high sulfate values (∿0.40% w/w sulfate sulfur) were found on this coal which was stored for sometime after grinding. The objective was to determine if the sulfate was due to weathering of the as-received 1-1/2" x 0 coal or the result of post-grinding storage. A representative sample of the coal pile was taken at the storage area and particle size fractions were obtained from the sample to determine the extent of weathering for three fractions after grinding to 3/8" topsize (3/8" x 14 mesh; 14 x 100 mesh; 100 mesh x 0).

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*Standard starting leach solution contains 18% Ferric Sulfate (5% Fe), 4% acid, 78% $H_2O$.

## TABLE 30. BENCH-SCALE PROCESSING OF MARTINKA COAL

| Experiment No. | Temp (°C) | Time (Hrs) | $O_2$ Pressure (psi) | $Fe^{+++}$ (%) | $H_2SO_4$ (%) | Coal Analysis, % w/w | | | | | Heat Content (Btu/lb) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Ash | Total Sulfur $S_t$ | Pyritic Sulfur $S_p$ | Sulfate Sulfur $S_s$ | Organic Sulfur $S_o$ | |
| Control RTU Processed Exp. 01-10 | 132 | -- | -- | 5 | 4 | --- | 0.91 | 0.17 | 0.12 | 0.65 | --- |
| 1* | 135 | 12 | 72 | 0 | 2 | 15.76 | 0.91 | 0.23 | 0.17 | 0.51 | 12360 |
| 2* | 135 | 12 | 72 | 0 | 0 | 16.15 | 0.90 | 0.20 | 0.01 | 0.69 | 12509 |
| 3** | 102 | 48*** | 0 | 5 | 20 | 11.80 | 0.96 | 0.29 | 0.06 | 0.61 | 13456 |

* Processed at 100 psig.

** Processed at ambient pressure.

*** Equivalent to ~ 14 hours @ 135°C.

Analytical data are summarized in Table 31. Included in the Table are similar data for the two additional RTU coals (designated RTU #2 and RTU #3) which were received from the mine in July 1977. Comparing RTU 1* with RTU 2* and RTU 3* in Table 31, it is seen that a significant decrease in pyritic sulfur and an increase in sulfate sulfur occurs for RTU 1.*

The data indicate that the majority of the observed weathering in the RTU ground coal occurred prior to the grinding operation. Additionally, the weathering is not a pile surface phenomenon since it is seen that the RTU 1 (Interior) sample likewise shows decreased pyritic sulfur and increased sulfate sulfur.

Elemental sulfur analyses of coals processed in the program studies have been included in Table 32. Samples of nonprocessed input coal were ground to 14 mesh and extracted with toluene to remove elemental sulfur. It is seen that uniformally sampled RTU coals have 0.03% w/w elemental sulfur whereas Kentucky Mine No. 9 coal (a Gravichem coal) has 0.10% w/w elemental sulfur. These data show that elemental sulfur is produced during weathering, however, not to the extent that is is produced ($\sim$0.4% w/w $\Delta S_p$) during Meyers Processing.

During the RTU coal sampling studies it was noted (Table 32) that random (yellow) deposits were present throughout the coal pile. Sampling of these deposits with subsequent processing for removal of elemental sulfur revealed the presence of higher than normal elemental sulfur. Additionally, qualitatively, high presence of sulfate was determined.

### 7.3.4 Density of Coal Slurry

A series of density determinations were made on 100 mesh x 0 and 14 mesh x 0 Martinka mine cleaned coal in slurry concentrations ranging from 19% to 42% coal by weight in distilled water. Densities of the slurry combinations are tabulated in Table 33. It is seen, in addition, that the average density of the 14 mesh x 0 coal is 1.4241 gm/cc ±0.0052 gm/cc. Similar values for the 100 mesh x 0 coal (1.4221 gm/cc ±0.0053 gm/cc) indicate that comparable wetting of the coal is achieved for both size distributions.

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*Ground to 3/8" x 0 before separation into fractions.

TABLE 31. DISTRIBUTION OF INORGANIC SULFUR IN RTU COALS (%)

| Coal | Combined Coal Fractions | | 3/8" x 14 Mesh | | 100 Mesh x 14 | | 100 Mesh x 0 | |
|---|---|---|---|---|---|---|---|---|
| | $S_p$* | $S_s$** | $S_p$ | $S_s$ | $S_p$ | $S_s$ | $S_p$ | $S_s$ |
| RTU 1*** | 0.92 | 0.59 | 0.78 | 0.44 | 0.66 | 0.50 | 1.88 | 1.3 |
| RTU 1 (Interior) | 0.70 | 0.58 | -- | -- | -- | -- | -- | -- |
| RTU 2*** | 1.16 | 0.01 | 1.05 | 0.01 | 1.00 | 0.11 | 2.18 | 0.36 |
| RTU 2 (Interior) | 1.16 | 0.01 | -- | -- | -- | -- | -- | -- |
| RTU 3*** | 1.02 | 0.05 | 0.82 | 0 | 0.92 | 0 | 2.00 | 0.11 |
| (COAL SIZE FRACTIONS) | | | | | | | | |
| RTU 1 | | | 58 | | 26 | | 16 | |
| RTU 1A | | | 51 | | 18 | | 6 | |
| RTU 2 | | | 63 | | 25 | | 13 | |
| RTU 3 | | | 67 | | 22 | | 11 | |

* $S_p$ = Pyritic Sulfur

** $S_s$ = Sulfate Sulfur

*** Ground to 3/8" x 0 before separating into fractions

TABLE 32. ELEMENTAL SULFUR CONTENT OF NONPROCESSED COAL

| Coal* | Elemental Sulfur, % w/w |
|---|---|
| RTU 1** | 0.01 |
| RTU 2** | 0.02 |
| RTU 3** | 0.03 |
| Kentucky Mine No. 9** | 0.10 |
| RTU 1 (Yellow)*** | 0.07 |
| RTU 2 (Yellow)*** | 0.10 |

*Toluene extracted to remove elemental sulfur

**Uniform sampling

***Specially sampled yellow deposits

### 7.3.5 Elemental Sulfur Recovery

The product elemental sulfur from the oxidation of pyrite in coal by the Meyers Process has been routinely recovered by extraction with toluene and subsequent distillation of the solvent. Sulfur recovery is virtually complete by a single stage extraction of leached coal with toluene provided the coal is predried or azeotropically dewatered. Experimentation has demonstrated that acetone is preferable to toluene for product sulfur recovery because (a) it does not require that the coal be dewatered prior to recovery, (b) it extracts iron sulfates as well as elemental sulfur from wet coal, and (c) it is easily (56°C) and completely (>99.5%) recoverable from coal. Acetone has been selected as the most cost effective technique for elemental sulfur recovery from Meyers Process leached coal.

Investigations on acetone efficiency in recovery of product elemental sulfur, $S_n$, from the oxidation of pyrite in coal (Meyers Process) was performed at bench-scale with bench-scale leached and RTU leached Martinka coal samples. Parameters examined for appreciable effect on recovery efficiency were: (a) the moisture content of leached coal and feed solvent (from 1% to 72% water based

## TABLE 33. DENSITY OF COAL/WATER SLURRIES

| Coal Size (Mesh) | Slurry Concentration % | Temp °C | Density of Slurry (gm/cc) | Density of Coal (gm/cc) |
|---|---|---|---|---|
| 14 | 21 | 40 | 1.0594 | 1.4265 |
| | | 60 | 1.0510 | 1.4187 |
| | | 80 | 1.0418 | 1.4235 |
| | 28 | 40 | 1.0849 | 1.4325 |
| | | 60 | 1.0768 | 1.4256 |
| | | 80 | 1.0685 | 1.4301 |
| | 42 | 40 | 1.1363 | 1.4243 |
| | | 60 | 1.1286 | 1.4171 |
| | | 80 | 1.1215 | 1.4190 |
| | | | | $\bar{x}$ 1.4241 |
| | | | | $\sigma$ 0.0052 |
| 100 | 23 | 40 | 1.0920 | 1.4260 |
| | | 60 | 1.0835 | 1.4161 |
| | | 80 | 1.0760 | 1.4241 |
| | | | | $\bar{x}$ 1.4221 |
| | | | | $\sigma$ 0.0053 |

### EQUATIONS FOR CALCULATING DENSITY (D), gm/cc

| Slurry % | Function of Temp, °C | Temp °C | Function of Slurry Concentration % |
|---|---|---|---|
| 21 | D = 1.07713 - 0.00044 Temp | 40 | D = 0.9824 + 0.00366 Slurry |
| 28 | D = 1.10133 - 0.00041 Temp | 60 | D = 0.9734 + 0.00370 Slurry |
| 42 | D = 1.15100 - 0.00037 Temp | 80 | D = 0.9622 + 0.00379 Slurry |

on dry coal weight*), (b) coal particle size (14 and 100 mesh top-size), (c) extraction residence time per stage (0.5, 1.0, and 2.0 hours), (d) number of extraction stages (1 to 3), and (e) sample prehistory. The latter included leached coal samples extracted immediately after taken from the RTU belt filter (water rinse only) and samples that were stored for as long as 30 days; the study also included thoroughly washed coal samples and oven dried samples. The majority of experiments were performed with 14 mesh top-size, RTU leached coal slurried in twice its dry weight acetone. This coal contained 0.30 grams elemental sulfur per 100 grams of dry coal; one of the bench-scale leached Martinka coals contained 0.40% elemental sulfur. Acetone extractions were performed at the reflux temperature of the slurry (56°C).

The data generated in elemental sulfur recovery by acetone investigations are summarized in Table 34 and Figures 31 and 32. Table 34 presents data from 19 experiments involving two-and three-stage extractions of leached coal with acetone. Data are also presented from toluene extractions of dry leached coal for comparison purposes. The table shows the estimated weight of elemental sulfur and of moisture on 100 weights (dry basis) of leached coal fed to the first extraction stage (columns 2 and 3), the weight of the input sulfur recovered in each of the three stages, the total $S_n$ recovered, and the percent recovery (recovery efficiency). The elemental sulfur on the feed coal (leached coal) was estimated by three independent techniques: (1) the sulfur recovered by three toluene extractions, (2) forty percent of the chemically leached pyrite, and (3) from the increase in organic sulfur of leached but not extracted coal; the three techniques agreed within 10%. The asterisked experiments were performed with leached coal which was not completely washed from the iron sulfate reagent; thus, it is conceivable that a small quantity of sulfate sulfur may have been analyzed as elemental sulfur which could have exaggerated slightly the quoted efficiencies.

Figure 31 depicts the expected elemental sulfur recovery efficiencies, as a function of acetone extraction stages, from up to 14 mesh top-size chemically leached Martinka coal. The data were generated at reflux temperatures with

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*Water was present on the feed coal and in a limited number of experiments in the acetone feed.

## TABLE 34. PRODUCT ELEMENTAL SULFUR RECOVERY FROM LEACHED MARTINKA COAL

| | Sulfur ($S_n$), Grams, Per 100 Grams of Coal | | | | | | |
|---|---|---|---|---|---|---|---|
| Experiment No. | Estimated $S_n$ on Coal (% w/w) | Moisture on Feed Coal (% w/w) | 1st Stage Extraction $S_n$ Recovered | 2nd Stage Extraction $S_n$ Recovered | 3rd Stage Extraction $S_n$ Recovered | Total $S_n$ Recovery (% w/w) | % Recovery |
| **A. Acetone Extractions** | | | | | | | |
| 1** | 0.30 | 1 | 0.23 | 0.04 | - | 0.27 | 90 |
| 2** | 0.30 | 1 | 0.29 | 0.04 | 0.02 | 0.35 | 117 |
| 3 | 0.30 | 1 | 0.21 | 0.04 | - | .25 | 83 |
| 4** | 0.30 | 1 | 0.27 | 0.04 | - | 0.31 | 103 |
| 5 | 0.30 | 1 | 0.27 | 0.04 | 0.01 | 0.32 | 107 |
| 6 | 0.30 | 20 | 0.27 | 0.04 | - | 0.31 | 103 |
| 7 | 0.30 | 20 | 0.22 | 0.04 | 0.001 | 0.26 | 87 |
| 8 | 0.30 | 20 | 0.20 | 0.05 | - | .25 | 83 |
| 9 | 0.30 | 20 | 0.28 | 0.03 | 0.01 | 0.32 | 107 |
| 10 | 0.30 | 20 | 0.22 | - | - | - | - |
| 11 | 0.40 | 24 | 0.26 | 0.08 | 0.05 | 0.39 | 98 |
| 12 | 0.40 | 28 | 0.27 | 0.07 | 0.05 | 0.39 | 98 |
| 13 | 0.40 | 42 | 0.20 | 0.12 | 0.05 | 0.37 | 93 |
| 14 | 0.30 | 42 | 0.18 | - | - | - | - |
| 15 | 0.40 | 52 | 0.20 | 0.13 | 0.08 | 0.41 | 103 |
| 16 | 0.30 | 72 | 0.13 | - | - | - | - |
| 17 | 0.30 | 72 | 0.17 | - | - | - | - |
| 18 | 0.30 | 72 | 0.14 | - | - | - | - |
| 19 | 0.30 | 72 | 0.14 | - | - | - | - |
| **B. Toluene Extractions** | | | | | | | |
| 20 | 0.30 | 11 | 0.28 | 0.01 | - | 0.29 | 97 |
| 21 | 0.30 | 1 | 0.26 | 0.01 | - | 0.27 | 90 |

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[*] One hour extractions of 33% coal slurries at reflux temperatures (56°C for acetone slurries, 110°C for toluene).

[**] Filter belt water rinse only on process coal.

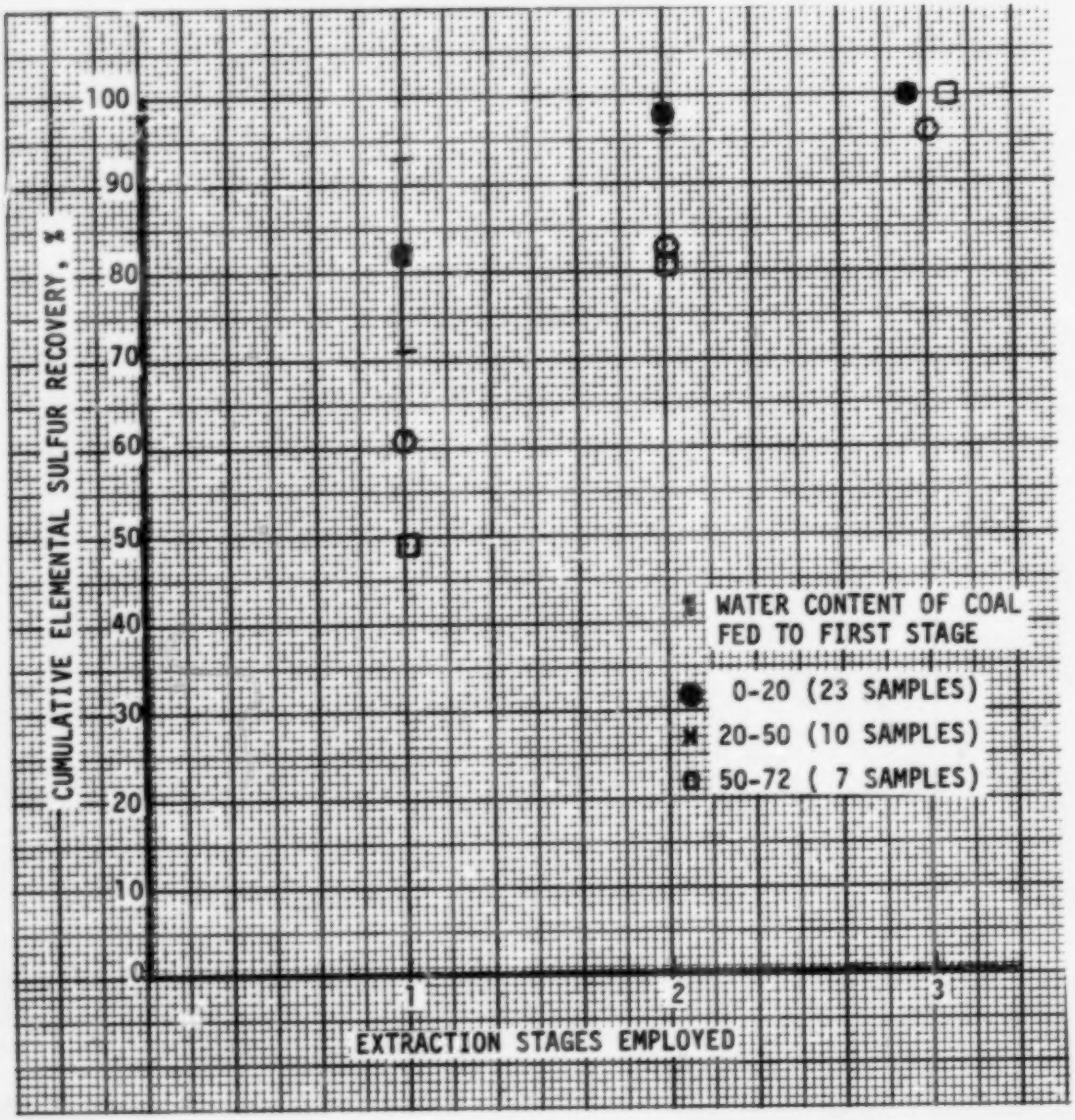


Figure 31. Elemental Sulfur Recovery as a Function of Acetone Extraction Stages

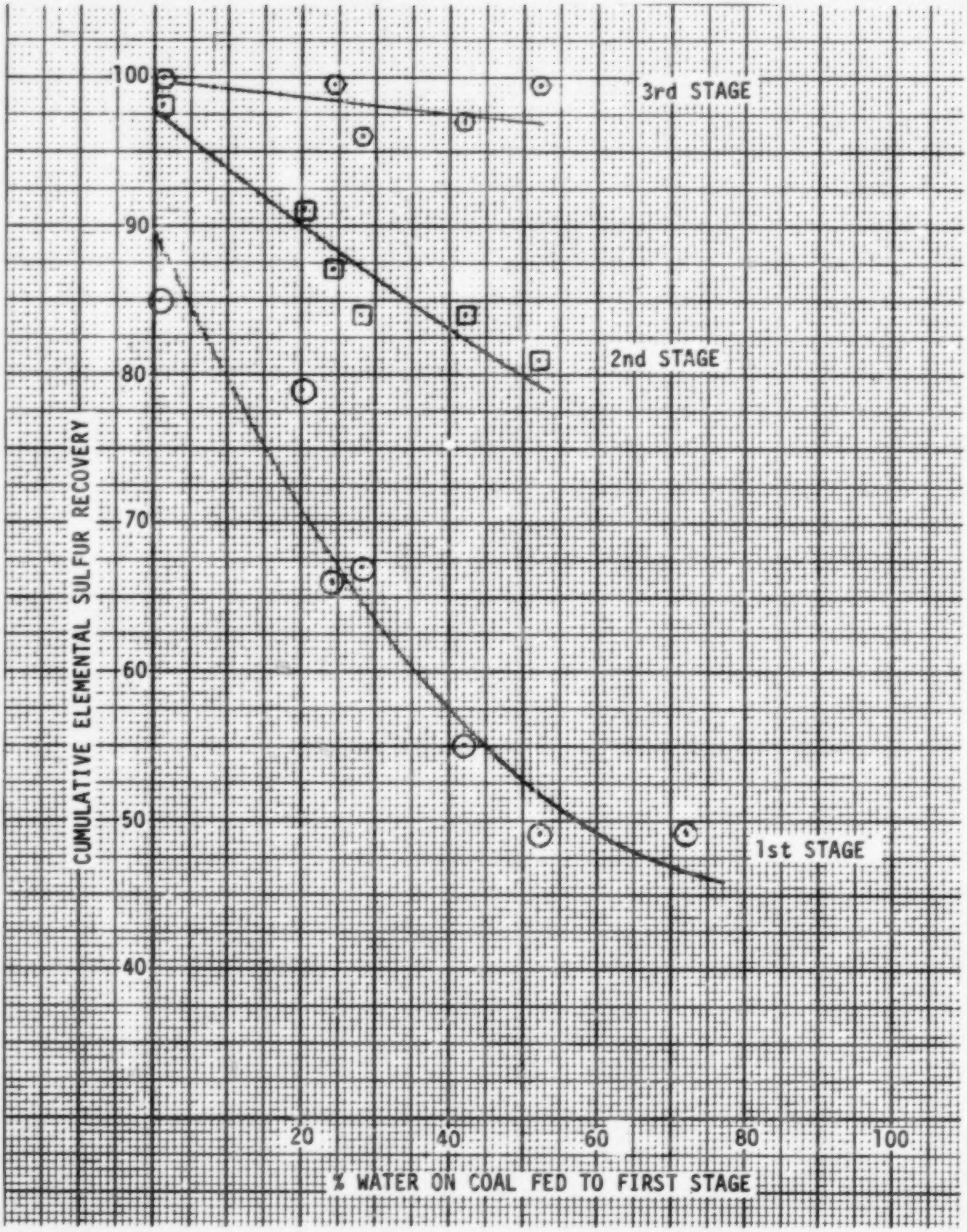


Figure 32. Effect of Water on Elemental Sulfur
Recovered by Successive Acetone Stages

coal which was leached chemically under a variety of conditions and up to 30 days prior to acetone extraction. Acetone extraction time was varied between 30 minutes and 2 hours per stage. The ±10 percent band about the first stage $S_n$ recovery value indicated for the 0-20 percent moisture coal samples applies also to the higher moisture coal samples also. This band represents the maximum uncertainty expected in the quoted average value and it is due partly to experimental and analysis uncertainties and partly to minor parametric effects (including effects due to small differences in water content). Similar or even larger relative uncertainties in the second and third extraction stages are masked by the small percentage of original elemental sulfur recovered in these stages.

Figure 32 summarizes the effect of water in the coal-acetone slurry on elemencal sulfur recovery from chemically leached coal. The moisture effect is depicted for each successive extraction stage.

The data presented here complemented with chemical analyses on the recovered elemental sulfur residues and determinations on acetone retention by extracted and dried coal led to the following observations:

- Elemental sulfur recovery from Meyers Process leached coal by a single stage acetone extraction ranged from 49% to 85% depending on the moisture content of the leached coal.
- The average elemental sulfur recovery by a single stage acetone extraction of processed coal containing 1-20% moisture was 83%. An additional 13% (approximately 80% of the residual $S_n$) was recovered in the second acetone extraction stage and another 2-3% in the third stage. The corresponding elemental sulfur recoveries from wet coal containing 50-70% moisture were 50, 30, and 20%.
- The water content of the chemically leached coal or of the feed (recycled) acetone had a pronounced effect on sulfur recovery efficiency during the first extraction stage. The moisture effect diminished in subsequent stages.
- Coal particle size up to 14 mesh top-size and extraction residence time beyond 30 minutes did not exhibit measurable effect on elemental sulfur recovery efficiencies by acetone.
- The purity of the sulfur ranged recovered from the first stage ranged between 50-80% and that of the second stage was between 40-60%; the sulfur content of the residue recovered in the third stage was approximately 10%.

- Approximately 0.5% of the coal matrix was dissolved in the three acetone extraction stages; at least 60% was dissolved in the first stage. The quantity of coal matrix dissolved in acetone appeared to be independent of the amount of sulfur recovered. Thus, product sulfur purity should increase with increasing pyrite concentration in the feed coal (higher concentration of product sulfur in the coal).

The above observations lead to the following conclusions:

- Elemental sulfur can be readily recovered from wet leached coal by acetone.

- Two 1-hour acetone extraction stages should be adequate for better than 85% sulfur recovery provided the water content of the acetone-coal slurry does not exceed 40% of the weight of the coal in the slurry. (A third stage may be required if the water concentration of the slurry is appreciably higher).

- Water concentration is the only parameter of those examined and in the ranges investigated that had a pronounced effect on elemental sulfur recovery by acetone.

- Acetone retention by the coal is expected to be less than 0.5% upon drying in commercial driers (extrapolation of data generated at TRW and at Wyssmont Co., Inc. laboratories).

- Acetone extraction is selective to elemental sulfur. Less than 0.5% of the coal matrix was dissolved in three stages of extraction (most of it was dissolved in the first stage).

## 7.4 LABORATORY STUDY CONCLUSIONS

1. Equilibrium float-sink separations of Martinka mine coal (14 mesh x 0) in ferric sulfate leach solution of varying specific gravity demonstrate the feasibility and the physical and chemical basis of the Gravichem method.

2. The sulfur content of Gravichem float and sink coal fractions is reduced during gravity separation because of leaching of pyritic sulfur.

3. Gravichem sink material has greatly enhanced heat content because of dissolution of coal mineral matter in addition to pyrite.

4. Equilibrium Gravichem processing of 3/8-inch top-size coal from Kentucky No. 9 Mine (TVA coal) generated a float product (38-52% w/w yield) containing 3.09-3.50 lbs $SO_2/10^6$ Btu, having a heat content range between 13774 and 14354 Btu/lb. This coal meets Tennessee State sulfur standards.

5. The sink fraction of the TVA coal when treated at 102°C according to Meyers process procedures, yields a coal containing less than 4 lbs $SO_2/10^6$ Btu.

6. Non-equilibrium Gravichem separation of coal into four fractions revealed that a greater yield of clean coal may be attained than was noted for simple float/sink fractions (two fractions).

7. Data from coal cleaning tests in the U.S.S.R. using ferric sulfate solution as the separation medium corroborates the TRW data and verifies the applicability of Gravichem as a Meyers process modification.

8. The amount of pyritic sulfur removal by chemical leaching is not affected by $Fe^{+++}$ and acid concentration under simultaneous coal leaching-reagent regeneration conditions.

9. High (20%) $H_2SO_4$ concentration does not change the response of inorganic sulfur to the oxidizing reaction of the Meyers process.

10. Weathering of RTU coals during storage prior to processing was observed. Weathering was manifested by reduction in the pyritic sulfur content of the coal, by increase in sulfate sulfur content, and by formation of elemental sulfur.

11. Elemental sulfur can be readily recovered from wet leached coal by acetone.

## 8. ENGINEERING DESIGN AND COST ESTIMATION

This section of the report documents the results of a process engineering study performed in support of the current RTU Project. The primary objectives of the process engineering effort were twofold:

1) To prepare conceptual full-scale process designs specific to several coal feed stocks incorporating updated process data from the RTU.
2) To evaluate the new Gravichem process option on a conceptual full-scale basis combining data obtained at lab or bench-scale with RTU plant data.

The detailed results of the current process engineering task are presented on the following pages.

Section 8.1 contains a brief introduction and the historical background which lead to the current chemical coal desulfurization process scheme. Also described in this section is the generalized Gravichem Process concept. The balance of Section 8.1 deals with the approach which was utilized in generating conceptual full-scale process designs, determining battery limits process capital and operating costs, and evaluating integrated grass roots process economics.

Section 8.2 details the specific base case designs, flow sheets, equipment lists, battery limits costs, and integrated grass roots facility costs and economics evaluations. Section 8.3 presents the data analysis conclusions drawn from the engineering effort.

### 8.1 INTRODUCTION AND BACKGROUND

Throughout bench-scale development, processing techniques and their associated costs have frequently been reviewed with an objective of focusing experimental effort in the areas of greatest cost sensitivity. The capital cost of equipment required to perform the pyrite leaching must be carefully controlled to maintain a low processing cost per ton of coal product. A considerable effort has been made to reduce costs in the core processing steps. While some improvements in cost have been made in the basic Meyers process compared to previous designs, the major emphasis has centered on obtaining the large cost advantages possible by gravity separation of coal into clean (float) and high pyrite (sink) fractions and chemically processing only the high pyrite fraction. The goal has therefore been to obtain maximum benefit from the new Gravichem float/sink technology presently under development. During the course of the current engineering task, two coal specific process designs were generated and evaluated. The designs incorporate Meyers process technology into recently demonstrated gravity separation techniques (which utilize Meyers process leach solution as a separation media) yielding improved desulfurization schemes defined as the "Gravichem Process". The two designs presented herein are specific to bench-scale and RTU tested mine cleaned Martinka coal and bench-scale tested TVA Kentucky Number 9 coal.

### 8.1.1 Historical Background

Over the last six years, there have been several process concepts developed by TRW which involve Meyers' Coal Desulfurization Process Technology. The earliest of the conceptual process designs was generated in 1972 and has been reported in detail previously(4). That design was based on processing a generalized 3.2% w/w pyritic sulfur ROM Lower Kittanning coal (pulverized to -100 mesh) in a batch mode to remove 95% w/w of the contained pyritic sulfur. The specific design was based on early laboratory-scale test data and the processing scheme represented a direct Meyers process treatment of coal.

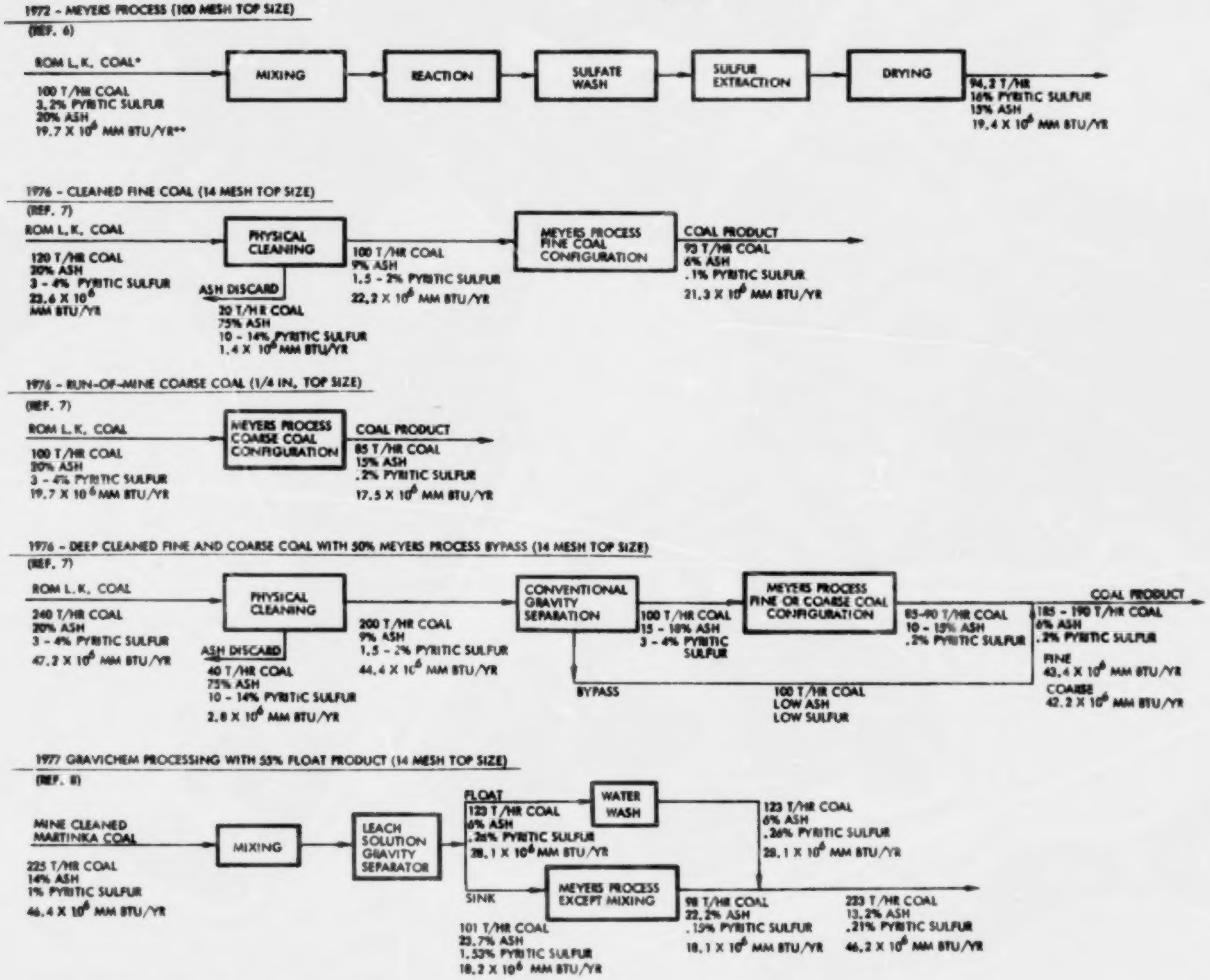
The next series of designs were generated in 1975 and 1976(5). Those designs also related to the desulfurization of a generalized ROM Lower Kittanning coal. However, the designs generated in that time period pertained to continuous mode coarse coal processing (0.25-inch top-size) and continuous mode fine coal processing (16 mesh x 0). Of the four design cases which were developed, one represented a straight-through Meyers Process, one involved a physical cleaning pretreatment and two of the schemes coupled physical cleaning, conventional gravity separation and Meyers process treatment.

The most recent of the reported bench-scale based design studies(11) was completed in late 1977. That design was specific to mine cleaned Martinka coal containing 1.2% w/w pyritic sulfur. The design was based on continuous mode operation utilizing 14 mesh x 0 coal. The overall process design incorporated Meyers process treatment with the newly developed float/sink gravity separation technology which utilized a 1.3 specific gravity Meyers process leach solution as the liquid media and takes advantage of concurrent pyrite leaching. The overall process is termed the Gravichem Process. This technology differs from the previous float/sink Meyers Process option(5) in that the conventional separation technique utilizes stabilized magnetite water solutions as the liquid media thus requiring a separate processing circuit. A series of block diagrams is presented in Figure 33 which indicate the genesis of the current process technology scheme.

### 8.1.2 Current Generalized Process Concept

As mentioned in the preceding paragraphs, the most recent generalized coal desulfurization processing technique, Gravichem, utilizes the previously demonstrated Meyers Process in conjunction with a newly developed leach solution gravity separation approach. A block diagram of the Gravichem Process is presented as Figure 34. It should be noted that the block diagram presents a processing concept which is generally applicable to any high pyrite containing suspendable coal (nominally 14 mesh top size). The scheme presented in Figure 34 represents the current state of Gravichem Process technology. It is based on past developmental experience(4,5,11) as well as information obtained during the current RTU program and its associated laboratory/bench scale support activities (discussed in Sections 6 and 7 of this report). The following paragraphs describe the Gravichem Process (Figure 34) and discuss the interconnections between each of the main process operations.

Ground coal, with a nominal top-size of 14 mesh, is mixed with hot recycled leach solution. Process required make-up sulfuric acid is also added to the mix tank such that the final leach solution specific gravity is maintained at the desired level. After coal wetting and mixing is complete at the solution boiling temperature, the now partially reacted coal slurry is cooled and introduced into a float/sink separator. The lighter low pyrite, low ash, coal particles float to the top of the separator in a relatively dilute slurry while the more dense high pyrite, high ash, coal particles in a much thicker slurry are pumped from the bottom of the unit.


1972 - MEYERS PROCESS (100 MESH TOP SIZE)
(REF. 6)
ROM L.K. COAL*
100 T/HR COAL
3.2% PYRITIC SULFUR
20% ASH
19.7 X 10⁶ MM BTU/YR**
MIXING
REACTION
SULFATE WASH
SULFUR EXTRACTION
DRYING
94.2 T/HR
16% PYRITIC SULFUR
15% ASH
19.4 X 10⁶ MM BTU/YR
1976 - CLEANED FINE COAL (14 MESH TOP SIZE)
(REF. 7)
ROM L.K. COAL
120 T/HR COAL
20% ASH
3 - 4% PYRITIC SULFUR
23.6 X 10⁶ MM BTU/YR
PHYSICAL CLEANING
ASH DISCARD
20 T/HR COAL
75% ASH
10 - 14% PYRITIC SULFUR
1.4 X 10⁶ MM BTU/YR
100 T/HR COAL
9% ASH
1.5 - 2% PYRITIC SULFUR
22.2 X 10⁶ MM BTU/YR
MEYERS PROCESS FINE COAL CONFIGURATION
COAL PRODUCT
93 T/HR COAL
6% ASH
.1% PYRITIC SULFUR
21.3 X 10⁶ MM BTU/YR
1976 - RUN-OF-MINE COARSE COAL (1/4 IN. TOP SIZE)
(REF. 7)
ROM L.K. COAL
100 T/HR COAL
20% ASH
3 - 4% PYRITIC SULFUR
19.7 X 10⁶ MM BTU/YR
MEYERS PROCESS COARSE COAL CONFIGURATION
COAL PRODUCT
85 T/HR COAL
15% ASH
.2% PYRITIC SULFUR
17.5 X 10⁶ MM BTU/YR
1976 - DEEP CLEANED FINE AND COARSE COAL WITH 50% MEYERS PROCESS BYPASS (14 MESH TOP SIZE)
(REF. 7)
ROM L.K. COAL
240 T/HR COAL
20% ASH
3 - 4% PYRITIC SULFUR
47.2 X 10⁶ MM BTU/YR
PHYSICAL CLEANING
ASH DISCARD
40 T/HR COAL
75% ASH
10 - 14% PYRITIC SULFUR
2.8 X 10⁶ MM BTU/YR
200 T/HR COAL
9% ASH
1.5 - 2% PYRITIC SULFUR
44.4 X 10⁶ MM BTU/YR
CONVENTIONAL GRAVITY SEPARATION
100 T/HR COAL
15 - 18% ASH
3 - 4% PYRITIC SULFUR
BYPASS
100 T/HR COAL
LOW ASH
LOW SULFUR
MEYERS PROCESS FINE OR COARSE COAL CONFIGURATION
85-90 T/HR COAL
10 - 15% ASH
.2% PYRITIC SULFUR
COAL PRODUCT
185 - 190 T/HR COAL
6% ASH
.2% PYRITIC SULFUR
FINE
43.4 X 10⁶ MM BTU/YR
COARSE
42.2 X 10⁶ MM BTU/YR
1977 GRAVICHEM PROCESSING WITH 55% FLOAT PRODUCT (14 MESH TOP SIZE)
(REF. 8)
MINE CLEANED MARTINKA COAL
225 T/HR COAL
14% ASH
1% PYRITIC SULFUR
46.4 X 10⁶ MM BTU/YR
MIXING
LEACH SOLUTION GRAVITY SEPARATOR
FLOAT
123 T/HR COAL
6% ASH
.26% PYRITIC SULFUR
28.1 X 10⁶ MM BTU/YR
WATER WASH
123 T/HR COAL
6% ASH
.26% PYRITIC SULFUR
28.1 X 10⁶ MM BTU/YR
SINK
101 T/HR COAL
23.7% ASH
1.53% PYRITIC SULFUR
18.2 X 10⁶ MM BTU/YR
MEYERS PROCESS EXCEPT MIXING
98 T/HR COAL
22.2% ASH
.15% PYRITIC SULFUR
18.1 X 10⁶ MM BTU/YR
223 T/HR COAL
13.2% ASH
.21% PYRITIC SULFUR
46.2 X 10⁶ MM BTU/YR

*ROM L.K. COAL = RUN-OF-MINE LOWER KITTANNING COAL
**[illegible] OPERATING HOURS PER YEAR, DRY COAL BASIS.

Figure 33. History of the Gravichem Process

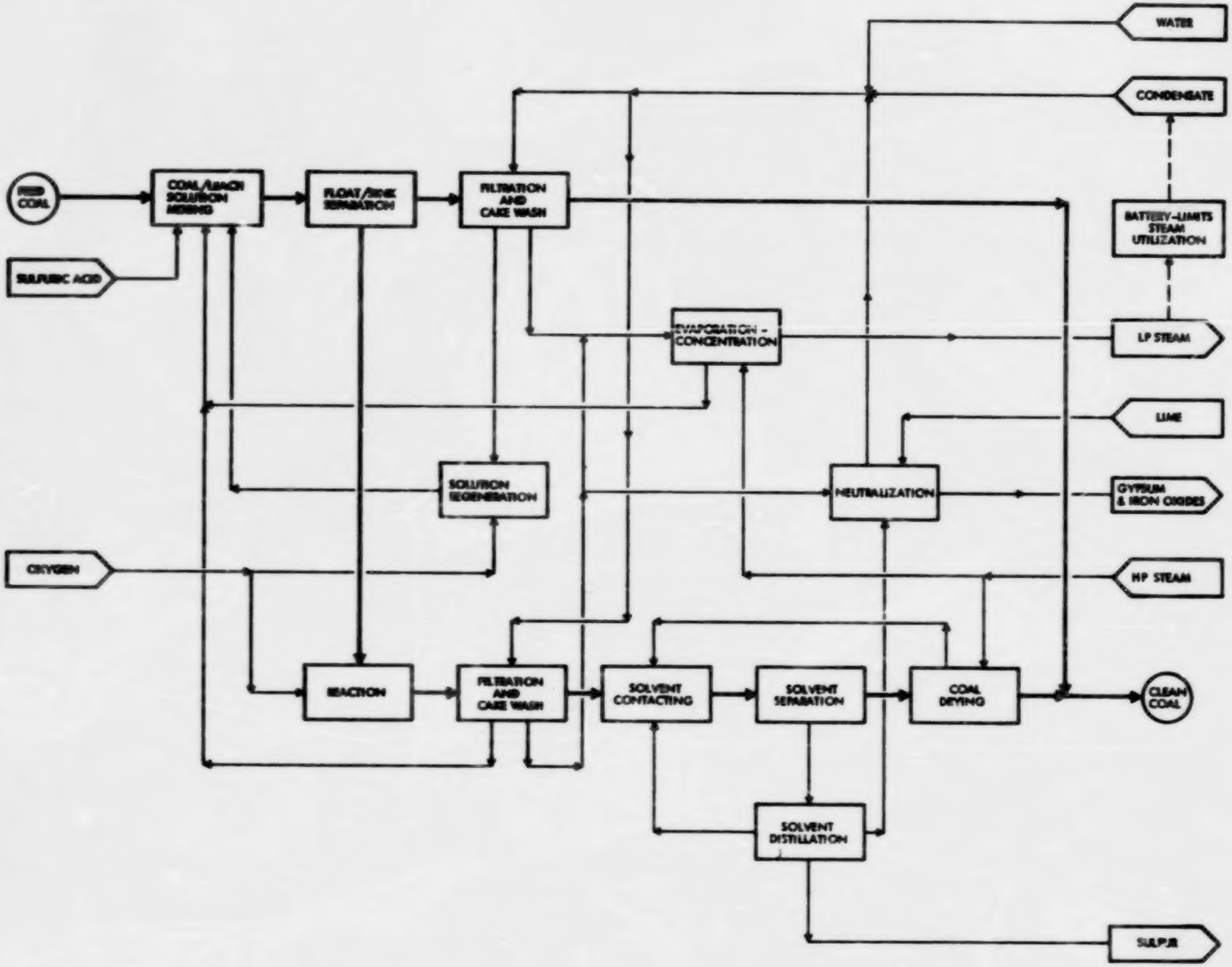

WATER
CONDENSATE
FEED COAL
COAL/LEACH SOLUTION MIXING
FLOAT/SINK SEPARATION
FILTRATION AND CAKE WASH
BATTERY-LIMITS STEAM UTILIZATION
SULFURIC ACID
EVAPORATION - CONCENTRATION
LP STEAM
LIME
SOLUTION REGENERATION
NEUTRALIZATION
GYPSUM & IRON OXIDES
OXYGEN
HP STEAM
REACTION
FILTRATION AND CAKE WASH
SOLVENT CONTACTING
SOLVENT SEPARATION
COAL DRYING
CLEAN COAL
SOLVENT DISTILLATION
SULFUR

Figure 34. Gravichem Process Block Diagram Suspendable Coal (14 mesh x 0) Approach

The clean (low pyrite, low ash) coal float fraction is next sent through a series of filtrations and water contacting operations to wash the iron sulfate-sulfuric acid leach solution from the coal. The washed coal cake is then ready for final blending into the chemically desulfurized sink fraction. The recombined fractions comprise the product coal stream. The float cake wash water is supplied from internally process generated steam condensate and make-up water. The concentrated leach solution filtrate is sent through a regenerator where the ratio of $Fe^{+3}$ to total Fe is adjusted via oxygen induced oxidation. The regenerated reagent stream is then recycled back to the mixing unit.

The high pyrite, high ash sink fraction from the separator is introduced into a reaction vessel. It is here that the majority of the exothermic pyrite leach reaction takes place at elevated temperatures and pressures in the presence of oxygen. The oxygen is simultaneously added to exothermally regenerate (adjust the $Fe^{+3}$ to total iron ratio) the leach solution.

The regenerated, fully reacted slurry is then subjected to a filtration and cake wash operation. The water used for sink cake washing is obtained from internally generated process steam condensate and make-up water. The concentrated leach solution filtrate is recycled directly to the mix tank. The wash filtrate (very dilute leach solution) is split with the majority of the steam going to the neutralization operation. It is during the neutralization operation that lime is added to the dilute leach solution stream to effect recovery of product iron and sulfate as a rusty gypsum. The remainder of the wash filtrate is concentrated via evaporation, mixed with the concentrated leach solution, and recycled to the mix tank. The steam generated during evaporation/concentration is utilized within the battery limits process in various process heating applications with the condensate being recycled as cake wash water. Utility purchased high pressure steam is used as the heat source for evaporation.

The water washed sink cake is next contacted with an appropriate organic solvent, namely acetone, to effect elemental sulfur extraction from the cake. The solvent rich coal slurry is then subjected to either filtration or centrifugation, depending on specific process requirements. The solvent – miscible water – elemental sulfur-sulfate sulfur solution is then separated from the acetone wet cake. The multi-component solution is then distilled under elevated pressure and temperature such that molten elemental sulfur is recovered for disposal. The recovered acetone is recycled to contacting while the sulfate laden water stream is sent to neutralization for sulfate removal and water recycle to cake wash operations.

The solvent wet sink cake is next sent through a drying operation where all but very small quantities of the acetone are flashed from the cake, condensed and recycled to solvent contacting. High pressure utility steam is used to heat the circulation inert gas ($N_2$) stripping media utilized in the dryer. The hot dry sink cake is next blended with the cooler water wet float cake to produce a low pyrite, reduced ash, Gravichem Process clean coal product.

### 8.1.3 Base Case Design, Cost Estimate, and Economics Approach

During the course of the current RTU project, two base case conceptual full scale process designs were generated. Base Case 1 is a process designed to treat mine cleaned Martinka coal, containing 1.51% w/w total sulfur (1.0% w/w pyritic sulfur) containing 2.3 lbs $SO_2$/MM Btu to a sulfur content level equivalent to 1.2 lbs $SO_2$/MM Btu. Base Case 2 is specific to the treatment of TVA Kentucky No. 9 coal. The TVA coal process objective was to decrease the initial 4.3% w/w total sulfur (2.4% w/w pyritic sulfur) containing 6.94 lbs $SO_2$/MM Btu coal down to an equivalent sulfur content of 4 lbs $SO_2$/MM Btu.

#### 8.1.3.1 Design Bases--

Presented in this section are the design bases and related assumptions which were utilized in generating the two base case conceptual full scale Gravichem Process designs. Unless otherwise noted, the information delineated below is common to both base cases.

**Feed Coal.**

**Base Case 1**

- 14 mesh x 0 coal from the Martinka Mine, Lower Kittanning seam.
- 225 TPH total coal feed rate, chosen such that 100 TPH is processed in leach reactor

- Coal contains 1.51% w/w total sulfur with 1% w/w pyritic sulfur
- 12,900 Btu/lb HHV
- 3% w/w moisture

Base Case 2

- 14 mesh x 0 TVA coal from Hopkins County, Kentucky Number 9 seam
- 200 TPH total coal feed rate such that 100 TPH is processed in each leach reactor
- Coal contains 4.3% w/w total sulfur with 2.4% w/w pyritic sulfur
- 12,400 Btu/lb HHV
- 10% w/w moisture

Product Coal.

- Base Case 1 combined float and sink coal to meet 1.2 lb $SO_2$/MM Btu specification
- Base Case 2 combined float and sink coal to meet 4.0 lb $SO_2$/MM Btu specification

Mixing.

- Coal slurry mixed to 25% w/w coal based on requirements for float/sink separation
- Coal mixed at 215°F for 45-minute residence time in agitated vessel. Based on RTU experience for adequate wetting and deaeration
- 3 stage mixer to ensure residence time
- Leach solution contains 7.5% w/w Fe and 4% $H_2SO_4$ resulting in a 1.3 specific gravity required for float/sink separation

Float/sink separation.

- One hour residence time in separator at 176°F based on bench-scale studies discussed in Section 5
- Coal fractons based on bench-scale experimentation (Section 5)

  Base Case 1 — 125 TPH float/100 TPH sink

  Base Case 2 — 100 TPH float/100 TPH sink

- Sink slurry is 33% w/w coal, float slurry is about 20% w/w coal based on information from suppliers of coal cleaning equipment and bench-scale studies

Reaction. The net overall reaction between pyrite and ferric sulfate leach solution is represented by:

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \rightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8\ S$$

$$\Delta H = -55 \text{ Kcal/g mole } FeS_2 = -0.10 \text{ MM Btu/lb mole } FeS_2 \text{ reacted}$$

The reaction rate, having second order dependence on the pyrite concentration and fraction of total iron as $Fe^{+3}$, is represented by the following empirical rate equation

$$r_L = \frac{-d[W_p]}{dt} = K_L\ K_R\ [W_p]^2\ [Y]^2$$

where

$W_p$ = wt % pyrite in coal at time t

$Y$ = fraction of total iron as ferric ion at time t

$K_L$ = leach rate constant (function of temperature and coal top size)

$K_R$ = reactor constant (function of reactor size, configuration, etc.)

Base Case 1

- 6-hour residence time in reactor at 250°F and 35 psig based on RTU experience and bench-scale determination of rate constants (Section 5 and Reference 11). Reaction rates were found to be higher in the RTU than those found at bench-scale thus requiring the use of $K_R$ in the rate expression.
- Extent of reaction carried out in the mixer and separator is based on rate constants determined at bench-scale adjusted for the respective temperatures.
- Extent of ash removal on the leached coal is based on the amount of pyrite reacted.

Base Case 2

- 6-hour residence time at 250°F and 35 psig based on bench-scale studies of TVA coal resulting in equal or faster reaction rates than Martinka coal. Reaction rate constants were adjusted by $K_R$ assuming the same increase in rate would be observed at larger scale on the TVA coal as was observed on Martinka coal at RTU scale.

- Extent of reaction in mixer and separator are based on bench-scale determined rate constants adjusted for the operating temperatures of the mixer and separator.

- Extent of ash removed is based on the amount of pyrite reacted although bench scale data (Section 7) indicates a removal of other ash on the processed sink coal. The implications of this difference are discussed in Section 8.3.1.

Regeneration. The regeneration of the leach solution is represented by the following reaction:

$$FeSO_4 + 0.5\ H_2SO_4 + 0.25\ O_2 \rightarrow 0.5\ Fe_2(SO_2)_3 + 0.5\ H_2O$$

$$\Delta H = -18.6\ \text{Kcal/g-mole}\ FeSO_4 = 0.0335\ \text{MM Btu/lb-mole}\ FeSO_4$$

- Regeneration in the reactor at 250°F and 35 psig maintains a $Y = 0.95$ based on previously determined bench-scale data(4,5).

- 0.5-hour residence time in regenerator to maintain Y at 0.90 for recycled leach solution at the mixer based on bench-scale studies(4,5).

Filtration and cake washing. Based on RTU and bench-scale experimentation (Sections 7 and 8 and Reference 11) the filter/washing operation is modeled as follows:

- At the interface on the filter drum between filtration and cake washing the coal cake contains 50 pounds of water plus its associated salt per 100 pounds of coal.

- 90% of the salt remaining on the cake at the interface is surface salt which is removed by washing. The other 10% of the salt is in the coal pores and is not removed by cake washing.

- The minimum wash water required is equal to 1.4 times the amount of water on the coal cake at the interface.

- The "dry" coal cake contains 50 pounds water plus the residual salt per 100 pounds of coal.

- Subsequent reslurrying of the coal cake with water dilutes the salt contained in the coal pores to a homogeneous solution of salt and water which can be removed by additional filtration and washing.

Evaporation.

- Water removal carried out to the extent that recycled leach solution contains 7.5% w/w iron.

- Evaporator operated at 290°F and 35 psig such the steam produced can be utilized for process heating requirements.

Solvent contacting.

- The water washed coal cake is contacted with acetone to make up a slurry which is 40% by weight coal.

- Pore moisture and salt comes to equilibrium with the acetone, based on bench-scale experimentation (Section 7).

Solvent separation.

Base Case 1

- Elemental sulfur on coal is reduced to 0.08% w/w based on bench-scale studies (Section 1).

- Final separation of coal by centrifuge reduces acetone on coal cake to 12% w/w based on vendor supplied information (Bird Machine Co.).

Base Case 2

- Elemental sulfur on coal reduced to 0.2% w/w based on bench-scale studies (Section 1).

- Final separation of acetone from coal by rotary pan filter resulting in a coal cake containing 27% w/w acetone (Bird Machine Co.).

Drying.

- Requires 3 driers each with 54 trays and 60-minute residence time based on vendor testing and experience (Section 9).

- Inert gas temperature of 400°F heating coal to 225°F.

- Residual dry coal acetone levels of 0.1% w/w were based on vendor testing (discussed in Section 9) and additional manufacturer supplied information. While the vendor tests indicated residual acetone levels of 0.5% w/w, Wyssmont Inc. personnel indicated that a residual level of 0.1% w/w acetone would be attainable through proper adjustment of dryer gas recirculating rate and temperature, and solids residence time.

Solvent distillation.

- Column operated at 15 psig and 250°F to keep elemental sulfur molten in bottoms.
- Column diameter sized to maintain 5 ft/sec vapor flow.
- Column height is 65 feet using 20 trays based on suppliers information (Artisan Industries).

Neutralization.

- Stoichiometric conversion of $H_2SO_4$ and iron sulfates to gypsum and iron oxides.

Materials of Construction.

Based on RTU experience, materials studies and supplier recommendations the following materials were determined suitable for the various leach solution-coal services:

- Fiber reinforced plastics and elastomers up to 180°F.
- 316 L stainless up to atmospheric boiling temperatures (215°F).
- Hastelloy C and rubber/acid brick lined carbon steel for service up to 265°F.
- Titanium for service up to 300°F.

#### 8.1.3.2 Battery Limits Process Costs--

For each of the base case designs generated, a battery limits capital and operating cost was determined. Equipment lists, tabulating the required major equipment were generated. The associated equipment numbers presented on the lists are keyed to the process flow diagrams. The selected equipment was sized to approach the optimum cost for processing the specific coal to the desired product sulfur content.

Battery limits capital cost. Capital equipment costs adjusted to mid-1978, were obtained from various sources: technical literature, equipment suppliers and internal (TRW) costing data. The specific sources of data for the various classes of equipment are presented in Table 35. When cost data were obtained from literature or other noncurrent sources, appropriate cost escalation factors, based on the Marshall and Swift Equipment Cost Index (to escalate costs from date of publication to mid-1978), were applied. The capital equipment cost is also tabulated on the equipment list. The costs are presented in terms of FOB equipment cost and installed equipment cost. The FOB equipment cost is the base, uninstalled cost at point of manufacture or point of shipment. The installed equipment cost includes the following elements:

- FOB Equipment Cost
- Field Materials
    - Equipment
    - Piping
    - Concrete
    - Steel
    - Instruments
    - Electrical
    - Insulation
    - Paint
- Material Erection
- Direct Field Labor
- Indirect Costs
    - Freight
    - Taxes
    - Construction Overhead
    - Fringe Benefits
    - Labor Burden
    - Field Supervision
    - Temporary Facilities
    - Construction Equipment
    - Small Tools
    - Miscellaneous Field Costs
    - Contractor Engineering

The installed equipment cost does not include a contingency factor.

Battery limits process operating cost. The process operating costs have also been estimated for each of the base cost designs. The basis for these estimates was technical literature and informal supplier quotes. Specific sources of information are presented in Table 36. The total estimated battery limits processing cost was determined as presented in Table 37.

TABLE 35. SOURCES OF EQUIPMENT COST INFORMATION

| Equipment Type | Information Source |
|---|---|
| Hoppers | TRW Data |
| Conveyors | Reference 13 |
| Mixers | Reference 14 |
| Pumps | Reference 15 |
| Reactors | TRW Data |
| Vessels >40,000 gal | TRW Data |
| Vessels <40,000 gal | Reference 15 |
| Tanks >40,000 gal | TRW Data |
| Tanks <40,000 gal | Reference 15 |
| Drums | Reference 15 |
| Centrifuges and Support Equipment | Bird Machine Company |
| Filters and Support Equipment | Ametec Company |
| Heat Exchangers | Reference 15 |
| Evaporators | Reference 16 |
| Dryers and Support Equipment | Wyssmont Incorporated |
| Rotary Valves | Reference 15 |
| Separators | TRW Data |

#### 8.1.3.3 Overall Process Economics--

The overall Gravichem Process economics were evaluated for each of the base cases. The battery limit plants were incorporated with their associated off-sites so that integrated grass roots processing facilities could be defined. The following paragraphs describe the overall integrated Gravichem process model as well as the bases for the economic analyses performed.

TABLE 36. SOURCES OF OPERATING COST INFORMATION

| Cost Element | Information Source |
|---|---|
| Maintenance, Insurance, Taxes and Interest | Reference 14 |
| Labor Requirement (Number of Positions) | Reference 14 |
| Labor Cost | TRW Data |
| Utilities | |
| Electrical Power | TRW Data |
| Cooling Water | TRW Data |
| Process Water | Reference 14 |
| Materials | |
| Oxygen | Linde, Division of Union Carbide |
| Nitrogen | Linde, Division of Union Carbide |
| Sulfuric Acid | Reference 17 |
| Lime | Reference 17 |
| Acetone | Reference 17 |
| Waste Disposal | TRW Data |

Integrated facility description. The integrated desulfurization facility includes all battery limit Gravichem equipment plus the required off-sites. The off-sites include such items as:

- Feed and product coal storage, handling and transport equipment.
- Shallow physical coal cleaning facilities and size separation equipment.
- By-product handling and storage facilities.
- Waste treatment (physical cleaning and process generated) and storage facilities.
- Process water treatment, storage and pumping facilities.
- Cooling water treatment and pumping equipment.

TABLE 37. BATTERY LIMITS OPERATING COSTS FORMAT

| Capital Related Costs: | Annual Cost, $1000 |
|---|---|
| Depreciation — 10% straight line | XXXX |
| Maintenance, insurance, taxes interest — 15% of capital | XXXX |
| Labor: | |
| Labor, XX operating positions at $160,000/position | XXXX |
| Utilities: | |
| Electric power, XXX Kw at 5¢/Kw-hr | XXXX |
| Cooling water, XXXX gpm, 30°F rise at 5¢/1000 gal | XXX |
| Process water, XX gpm at 25¢/1000 gal | XX |
| Heating, XX MM Btu/hr, fired duty, XX TPH coal product equivalent | - |
| Materials: | |
| Oxygen, XX TPH at $50/ton | XXX |
| Nitrogen, XX TPH (included in oxygen cost) | - |
| Sulfuric acid, XX TPH at $55/ton | X |
| Lime, XX TPH at $35/ton | X |
| Acetone, X TPH at $320/ton | X |
| Waste disposal, X TPH at $6/ton | X |
| TOTAL COST | XXXXXX |

- Power and steam generation facilities
- Site office buildings and shop structures.
- Other site improvements such as roads, fences, railroad spurs, etc.

It should be noted that the economic evaluations presented herein do not include land costs and assume that oxygen and nitrogen is purchased as an over-the-fence utility item (i.e., neither battery limit nor off-site equipment include an oxygen plant). For an integrated process facility of this type, it has been estimated that the installed off-site capital cost will be equivalent to approximately 50% of the installed battery limits cost(18)

Process economics model. The technique used in capitalizing the integrated Gravichem process is the primary determinant in calculating the required unit price of the product. Due to the nature of the Gravichem process (clean energy production), only utility financing methods were considered in this evaluation. The specific method utilized in this analysis is based on the technique used by the Federal Power Commission Synthetic Gas-Coal Task Force in their report on synthetic gas(19). The recommended economic evaluation criteria are given in Table 38.

The annualized revenue expressions for utility financing which were developed by the FPC Task Force can be combined to give a simplified expression of the following form:

$$P = (0.140X + 0.121Y + 1.006Z)/E$$

where,

P = is the required sales price for processed coal, \$/MM Btu

X = working capital for raw materials and supplies, \$

Y = sum of the total plant investment and start-up cost, \$

Z = annual total operating cost, \$/year

E = annual energy output, MM Btu/yr

When this expression is utilized in conjunction with the criteria presented in Table 38, the required sales price for the processed coal is obtained. From the required sales price and the cost of the feed coal, an equivalent upgrading cost can be determined.

## TABLE 38. ECONOMIC EVALUATION CRITERIA UTILITY FINANCING*

Operating Cost Criteria

Raw material - coal at \$15/ton, \$20/ton, \$30/ton

Utilities

Electricity at 5¢/kw-hr
Oxygen at \$50/ton (nitrogen included in cost)
Cooling water at 5¢/1000 gal.
Process water at 25¢/1000 gal.

Chemicals

Lime at \$35/ton
Sulfuric acid at \$55/ton
Acetone at \$320/ton

Disposal at \$6.00/ton of refuse

Labor

Process operating labor at positions/shift x 8304 man-hours/yr x \$6/man-hour
Maintenance labor at 1.5%/yr of total plant investment
Supervision at 15% of operating labor and maintenance labor
General overhead and administration at 60% of labor and supervision

Supplies

Operating at 30% of process operating labor
Maintenance at 1.5% of total plant investment

Taxes and insurance at 3.7%/yr of total plant investment

Total operating cost = sum of raw material + utilities + chemicals + disposal + labor + supplies + taxes and insurance

---

*Assumes debt/equity = 75/25, interest on debt = 9%, return on equity = 15%.

(Continued)

TABLE 38. (Continued)

Capital Cost Criteria

Battery limits capital as discussed in text

Off-site capital at 50% of battery limits capital

Overhead and profit at 22% of battery limits + off-sites

Engineering and design at 10% of battery limits + off-sites

Contingency at 15% of battery limits + off-sites + overhead and profit + engineering and design

Total plant investment = sum of battery limits + off-sites + overhead and profit + engineering and design + contingency

Interest for construction at 9% of total plant investment x 1.875

Start-up cost at 20% of total operating costs

Working capital = sum of raw materials inventory of 60 days at full rate + materials and supplies at 0.9% total plant investment + 1/24 annual product revenue

## 8.2 DESIGN AND COST ESTIMATE BASE CASES

The following pages present the results of two process engineering studies relating to Gravichem application to two specific coal feedstocks. The coal feedstocks were mine cleaned Martinka Coal and TVA Kentucky No. 9 coal. Each of the base case designs are presented in terms of a brief process description, process flow diagrams, a major equipment list, battery limits process costs, and overall process economics. The detailed mass balance and their associated flow diagrams as well as steam balances for each of the design cases are presented in Appendix C.

### 8.2.1 Base Case 1 – Mine Cleaned Martinka Coal

Base Case 1 deals with a conceptual full-scale Gravichem Process design based on a processing facility capable of treating coal fed at a rate of 225 TPH from the Martinka Mine, Lower Kittanning seam. The coal has an "as received" heating value of 12,900 Btu/lb. The coal contains 1.51% w/w total sulfur with a pyritic sulfur level of 1.0% w/w. Process flow diagrams (Dwg. Nos. 2473-3 and 4) for the design are presented as Figures 35a and 35b. Presented on the flow diagrams are equipment, key process temperatures and pressures, flow rates and composition of selected coal streams, and flow rates for steam and raw materials.

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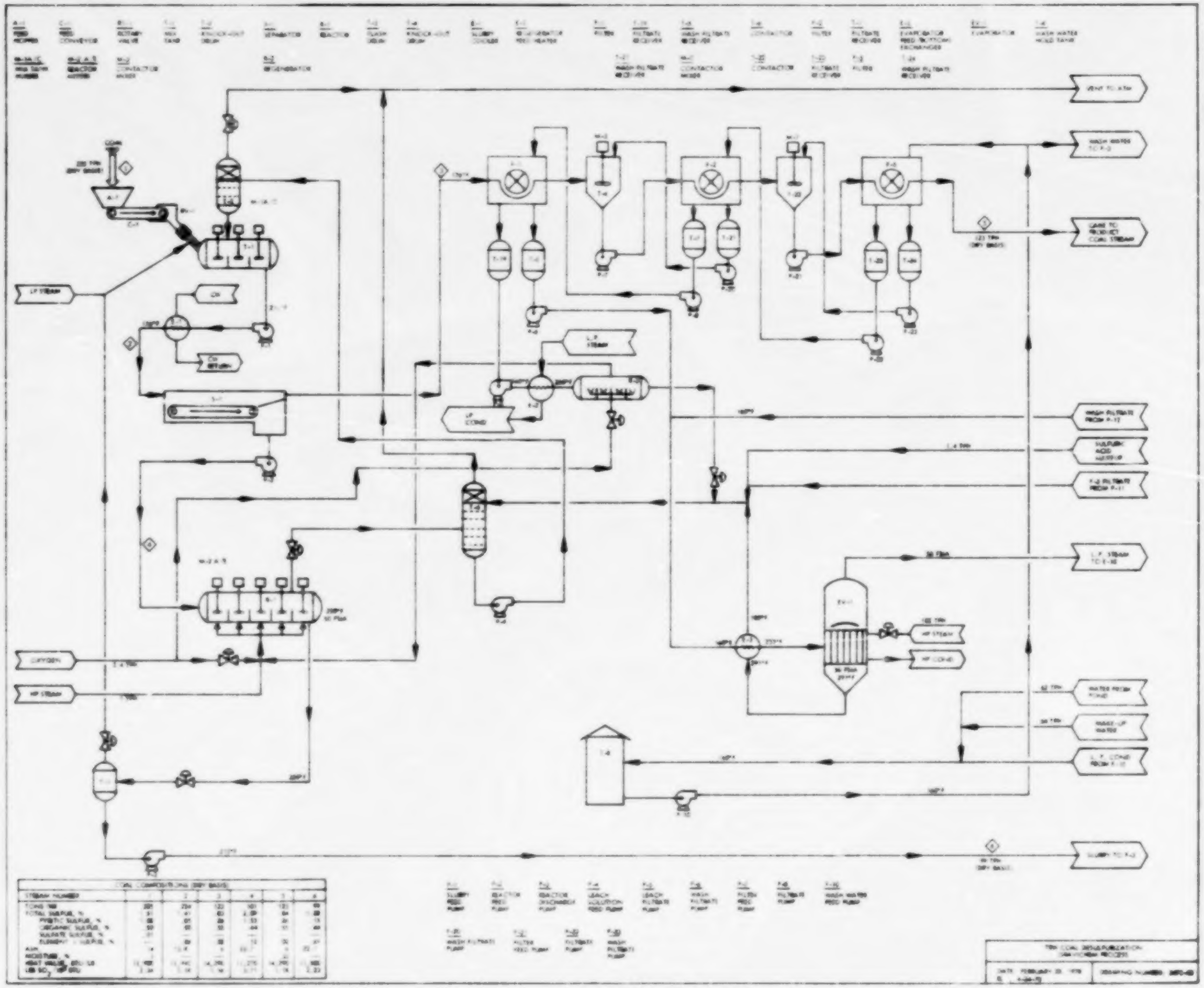
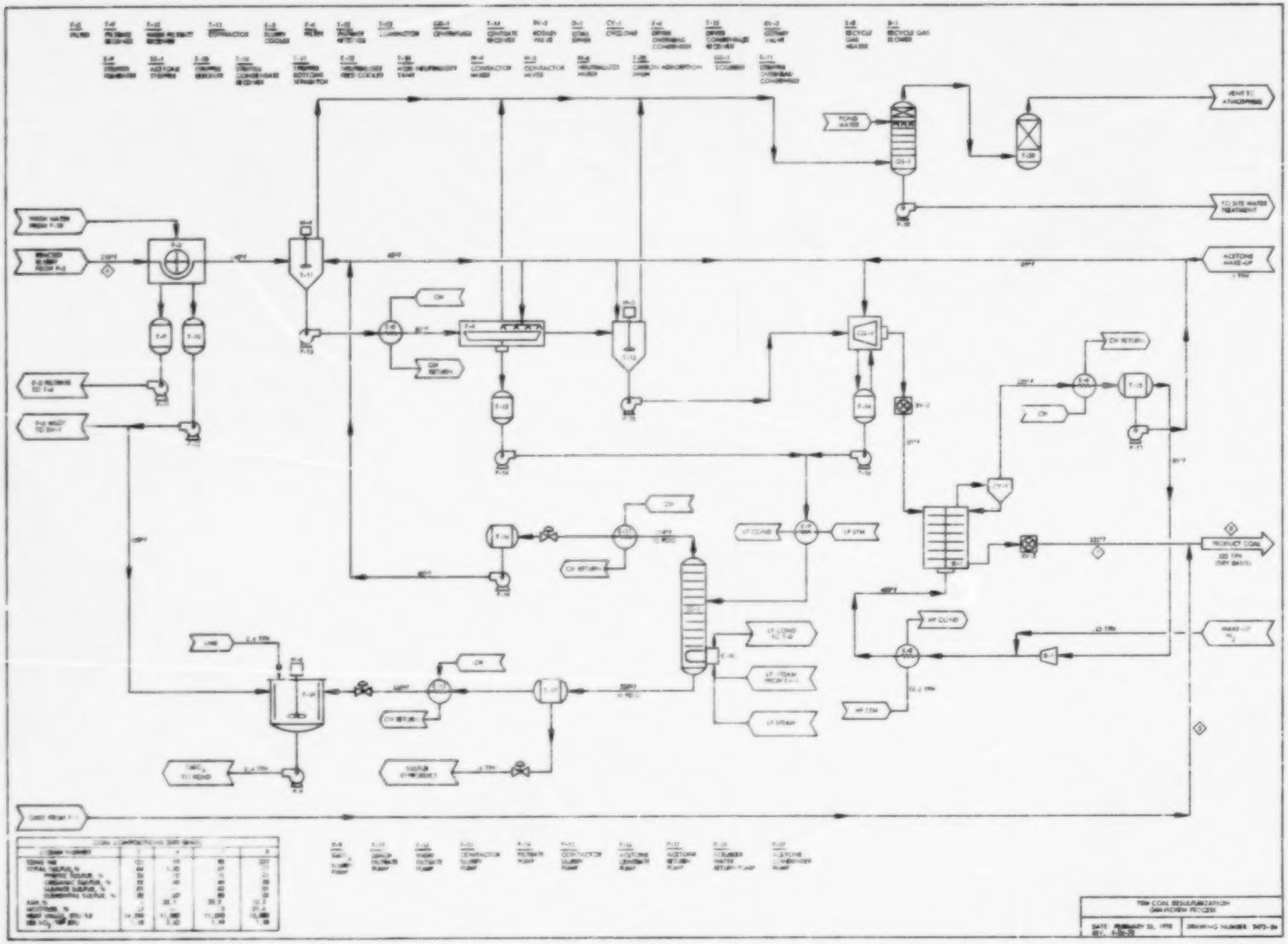

VENT TO ATM
WASH WATER TO F-3
SAME TO PRODUCT COAL STREAM
LP STEAM
L.P. STEAM
LP COND
WASH FILTRATE FROM P-12
SULFURIC ACID MAKEUP
F-2 FILTRATE FROM P-11
L.P. STEAM TO E-10
HP STEAM
HP COND
OXYGEN
HP STEAM
WATER FROM POND
MAKE-UP WATER
L.P. COND FROM E-10
SLURRY TO F-2
COAL COMPOSITIONS (DRY BASIS)
TRW COAL DESULFURIZATION GRAVICHEM PROCESS

Figure 35a. TRW Coal Desulfurization Gravichem Process


VENT TO ATMOSPHERE
POND WATER
TO SITE WATER TREATMENT
ACETONE MAKE-UP
PRODUCT COAL
222 TPH (DRY BASIS)
MAKE-UP $H_2$
TRW COAL DESULFURIZATION GRAVICHEM PROCESS
DRAWING NUMBER

MICROFILMED FROM
BEST AVAILABLE COPY

Figure 35b. TRW Coal Desulfurization Gravichem Process

#### 8.2.1.1 Process Description--

Feed and mixer. Crushed coal, nominally 14 mesh top-size, is fed from feed hopper A-1 to the mix tank T-1 by conveyor C-1. The coal, containing 1.0% w/w pyritic sulfur and 3% w/w moisture is fed at a rate of 225 TPH on a dry basis. Recycled leach solution at its boiling point (215$^{O}$F) is introduced to the first mixer stage after passing through the knock-out drum T-2. Flash steam from T-3 and low pressure steam are used to heat the coal on the conveyor to 215$^{O}$F. The mixer T-1 was sized for three stages at 0.25-hour residence time per stage to provide adequate wetting of the coal and partial reaction of the pyrite.

Separator. The slurry from the mixer which is 25% w/w coal is pumped through the slurry cooler to the separator S-1. The slurry is cooled to 176$^{O}$F in the slurry cooler E-1. The separator provides 1-hour residence time where the heavy pyrite rich coal will settle and the lighter low pyrite coal will float in the 1.3 specific gravity leach solution (see Section 7). Based on current bench scale desulfurization studies, about 55% of the coal feed will leave the separator as the float portion in a slurry which is about 21% w/w coal. After washing to remove leach solution, this coal will meet the total sulfur specification without further pyrite removal. The sink portion, containing 45% of the coal feed, is pumped to the primary reactor, R-1, as a 33% w/w coal slurry for further pyrite reduction.

Float coal washing and dewatering. The float slurry from the separator S-1 containing about 125 TPH coal is filtered, washed and recontacted with water in a 3-stage countercurrent arrangement of three filters (F-1, F-2 and F-5) and two contactors (T-6 and T-22). The coal cake from the last stage contains 33% w/w moisture and residual sulfate sulfur has been reduced to less than 0.01% w/w coal. The coal cake from this filter is the product coal from the float portion which will be recombined with the sink coal after it is processed for pyrite removal. The float coal contains 0.83% w/w total sulfur with a heating value of 14,290 Btu/lb, which is below the specification of 1.2 lb $SO_2/10^6$ Btu.

Primary reactor. The sink slurry from the separator containing about 100 TPH coal is pumped to the primary reactor R-1 where the leach reaction for the removal of pyrite takes place. The reactor was sized to provide 6-hour residence time at 250°F and 35 psig oxygen partial pressure which, based on RTU experimentations, will adequately remove pyrite to a level of 0.15% w/w pyritic sulfur in the coal (see Section 6). The reactor is maintained at 250°F by the generation of heat from heats of reaction and regeneration and the injection of 300 psig saturated steam into the reactor. The reactor is divided into 5 stages each with a mixer. Simultaneous regeneration of the leach solution to maintain a ratio of $Fe^{+3}$ to total iron equal to 0.95 is accomplished by feeding about 2 TPH oxygen to the reactor. The inert gas leaving the reactor is vented through a knock-out drum T-4 where it is contacted with recycled leach solution before venting to the atmosphere.

Sink coal filtration and washing. The slurry effluent from the reactor is flashed to about 1 psig and then pumped to the rotary drum vacuum filter F-3 where the leach solution is separated and the coal cake washed to remove residual sulfate salts. The wash water for the filter is recycled water from the wash water hold tank T-8. Make-up water from the pond is required. The coal cake from F-3 contains 33% w/w moisture.

Leach solution recycle loop. The wash filtrates from filters F-1 and F-3 containing iron sulfates are collected and fed to the evaporator EV-1 for water removal. In order to remove the excess iron produced from the leach reaction a portion of the wash filtrate F-3 is sent to the lime neutralizer for disposal. The evaporator feed stream is heated to 233°F in the feed/bottoms exchanger E-3. The evaporator is operated at 35 psig and about 290°F such that the water removed as steam may be used for process heating service. The leach solution in the evaporator bottoms is concentrated in iron to the extent that the recycled leach solution will be 7.5% w/w total iron at the mixer T-1. The filtrate from filter F-1 is heated to 250°F in exchanger E-2 and fed to the regenerator R-2. The regenerator R-2, operating at 250°F and 35 psig, is designed for 0.5-hour residence time to regenerate the F-1 filtrate such that the combined recycle streams will have a ratio of $Fe^{+3}$ to total iron equal to 0.90 at the mixer T-1. The oxygen requirement for the regenerator is about 0.25 TPH. The evaporator bottoms, regenerator effluent, F-3 filtrate and the makeup sulfuric acid are combined and fed to the knock-out drum T-4, then pumped to the mixer T-1 through knock-out drum T-2, thus completing the recycle loop.

Acetone washing and elemental sulfur removal. The coal cake from filter F-3 containing elemental sulfur produced in the leach reaction and residual sulfate salts from the leach solution is contacted with about 100 TPH of acetone in the contactor T-11. The coal slurry is then filtered on a rotary pan filter F-4 where the cake is washed with acetone. The coal cake from F-4 is again recontacted with acetone (110 TPH) in T-13 and the slurry fed to a centrifuge CG-1 where the resulting coal cake is reduced to about 12% w/w acetone. Bench-scale experience with two-stage acetone washing shows that the elemental sulfur on the coal is reduced to 0.08% w/w (see Section 7). The sulfate sulfur on the cake is reduced to about 0.02% w/w after the filter F-4. All of the acetone contacting equipment are vented to the atmosphere through a water scrubber GS-1 and carbon bed T-20 for residual acetone removal.

Acetone recovery and sulfur removal. The acetone streams from filter F-4 and the centrifuge CG-1 which contain elemental sulfur, water, and salts are preheated in E-9 and fed to the acetone stripper SS-1. The overhead vapor from the stripper, operating at 250°F and 15 psig, containing essentially all of the acetone feed is condensed and recycled to the contactor T-11. The stripper bottoms containing water, elemental sulfur and salts is fed to the stripper bottoms separator T-17 where the elemental sulfur is removed The sulfate rich solution is cooled by E-12 and fed to the neutralizer.

Lime Neutralization. The sulfate rich streams from the acetone stripper and the wash filtrate from F-3 are contacted with a lime slurry in the acid neutralizer T-18 where the sulfuric acid is neutralized and the salts reacted to produce gypsum. The gypsum slurry is dumped to a settling pond for disposal. Following settling, the pond water is returned to filter F-3 as part of the wash water following water treatment to remove any trace acetone.

Coal drying. The coal cake from the centrifuge CG-1 is fed through a rotary valve RF-2 to the coal drier D-1 where the coal is heated to 225°F by a 400°F nitrogen gas stream. The drier gas system is a closed loop with a condenser to remove the acetone, a recycle gas blower B-1, and two steam heaters E-7 and E-8 to heat the recycled nitrogen stream back to 400°F. The recovered acetone is returned to the system for further use. The dried coal from the drier is discharged through a rotary valve RV-3 and combined with the coal product from the float portion. The coal from the drier contains 0.69%

w/w total sulfur and has a heating value of 11,570 Btu/lb. The combined coal product contains 0.77% w/w total sulfur with a heating value of 13,080 Btu/lb resulting in 1.18 lb $SO_2/10^6$ Btu material.

### 8.2.1.2 Battery Limit Costs--

Equipment list. The previous paragraphs of this document presented a conceptual process design and flow diagram (Figures 35a and 35b) for a battery limits processing facility treating 225 TPH of feed coal (221.8 TPH of desulfurized coal product). An equipment list, tabulating the required major equipment, is presented in Table 39. The selected equipment was sized to process the 1.5% total sulfur feed coal such that the combined Gravichem product would contain no more than 1.2 lbs $SO_2$/MM Btu. As may be seen in Table 39, the total battery limits FOB equipment cost is 9.6 million dollars while the total installed equipment cost is 17.4 million dollars.

Battery limits process operating cost. Process operating costs have been estimated as presented in Table 40. This estimated total annualized operating cost results in an equivalent battery limit production cost of $6.61/ton of coal product. This production cost is based on an apparent product coal rate of 209.5 TPH (221.8 TPH of desulfurized product less 12.3 TPH for process steam generation). The battery limit processing facility therefore operates with an overall coal yield of 93% on a dry weight basis and an overall energy yield of 94% on a Btu basis. Also of interest is the net overall plant energy efficiency when the coal required for producing the electric power loads for the process and oxygen plant is accounted for along with the plant steam requirements. This efficiency, assuming a 33% efficiency for electric power from coal, is equal to 93.5% where the coal requirement for power production is 2.1 TPH. Another number of interest is the noncapitalized battery limits operating cost. This is essentially the total process operating cost less the annual depreciation charge (10% of installed equipment). The noncapitalized battery limit operating cost is $5.18/ton of coal feed (20¢/MM Btu equivalent) or $5.57/ton of coal product (21¢/MM Btu equivalent). The noncapitalized operating cost represents a pure operating cost of the battery limit plant.

## TABLE 39. BASE CASE 1 — PROCESS EQUIPMENT LIST

| | MAJOR PROCESS EQUIPMENT $9.64 MM FOB, $17.39 MM INSTALLED | $K FOB | $K Installed |
|---|---|---|---|
| A-1 | Feed Hopper - 11,000 ft$^3$ | 22 | 26 |
| B-1 | Recycle Gas Blower (3) - CS, 1.7 Compression Ratio, 40 hp | as D-1 | |
| C-1 | Feed Conveyor - 40 in. wide x 20 ft x 10 hp, 200 ft/min. | 16 | 27 |
| CG-1 | Centrifuge Package (2) - 44" ϕ x 132" Screen Bowl, CS, 200 ph | 599 | 1197 |
| CY-1 | Cyclone (3) - 5 psig, 850 ft$^3$, CS | as D-1 | |
| D-1 | Coal Dryer (3) - 30' ϕ 55', CS, 5 psig, 15 hp, 54 trays, 60 min. | 2100 | 2625 |
| E-1 | Slurry Cooler - 3550 ft$^2$, CS/SS | 80 | 217 |
| E-2 | Regenerator Feed Heater - 1840 ft$^2$, CS/Hastelloy C | 50 | 136 |
| E-3 | Evaporator Feed/Bottoms Exchanger - 4120 ft$^2$, Hastelloy C/Hastelloy C | 112 | 303 |
| E-5 | Slurry Cooler - 3400 ft$^2$, CS/SS | 78 | 212 |
| E-6 | Dryer Overhead Condenser (3) - 700 ft$^2$, CS/CS | as D-1 | |
| E-8 | Recycle Gas Heater (3) - 602 ft$^2$, CS/CS | as D-1 | |
| E-9 | Stripper Preheater - 125 ft$^2$, CS/SS | 13 | 48 |
| E-10 | Stripper Reboiler - 7,560 ft$^2$, Hastelloy C | 80 | 223 |
| E-11 | Stripper Overhead Condenser (2) - 9,420 ft$^2$, CS/CS | 260 | 780 |
| E-12 | Neutralizer Feed Cooler - 800 ft$^2$, CS/SS | 31 | 90 |
| EV-1 | Evaporator - 2000 ft$^2$, 35 psig, CS with titanium clad, 20 hp | 900 | 1440 |

(Continued)

TABLE 39. (Continued)

| | | $K FOB | $K Installed |
|---|---|---|---|
| F-1 | Rotary Drum Vacuum Filter Package (2) - 12' $\phi$ x 16', 608 ft$^2$, SS, 130 hp | 247 | 392 |
| F-2 | Rotary Drum Vacuum Filter Package (2) - 12' $\phi$ x 16', 608 ft$^2$, SS, 130 hp | 247 | 392 |
| F-3 | Rotary Drum Vacuum Filter Package - 12 $\phi$ x 24, 912 ft$^2$, SS, 250 hp (inc. vac. sys.) | 184 | 292 |
| F-4 | Rotary Pan Filter Package (2) - 24' $\phi$, 445 ft$^2$, SS, 105 hp (inc. vac. sys.) | 941 | 1491 |
| F-5 | Rotary Drum Vacuum Filter Package (2) - 12' $\phi$ x 16', 608 ft$^2$, SS, 130 hp | 247 | 392 |
| GS-1 | Scrubber - 5' $\phi$ x 30', 20 trays, 0 psig, CS | 13 | 21 |
| M-1 A/C | Mix Tank Mixers (6) - 25 hp, SS | 57 | 92 |
| M-2 A/E | Reactor Mixers (5) - 190 hp, Hastelloy C | 194 | 315 |
| M-3 | Contactor Mixer (2) - 25 hp, SS | 20 | 35 |
| M-4 | Contactor Mixer - 50 hp, SS | 13 | 21 |
| M-5 | Contactor Mixer (2) - 20 hp, CS | 8 | 14 |
| M-6 | Neutralizer Mixer - 15 hp, SS | 7 | 11 |
| M-7 | Contactor Mixer (2) - 25 hp, SS | 20 | 35 |
| P-1 | Slurry Feed Pump (2) -1500 gpm, 15 psi, 15 hp, SS | 15 | 45 |
| P-2 | Reactor Feed Pump - 1000 gpm, 15 psi, 10 hp, SS | 5 | 15 |

(Continued)

TABLE 39. (Continued)

|  |  | $K<br>FOB | $K<br>Installed |
|---|---|---|---|
| P-3 | Reactor Discharge Pump - 1000 gpm, 15 psi, 10 hp, SS | 5 | 15 |
| P-4 | Leach Solution Feed Pump (2) - 1100 gpm, 15 psi, 15 hp, SS | 8 | 21 |
| P-5 | Leach Filtrate Pump (2) - 600 gpm, 65 psi, 30 hp, SS | as F-1 |  |
| P-6 | Wash Filtrate Pump (2) - 300 gpm, 70 psi, 15 hp, SS | as F-1 |  |
| P-7 | Filter Feed Pump (2) - 550 gpm, 10 psi, 5 hp, SS | 4 | 13 |
| P-8 | Filtrate Pump (2) - 250 gpm, 7.5 psi, 2 hp, SS | as F-2 |  |
| P-9 | $CaSO_4$ Slurry Pump - 320 gpm, 4 hp, SS, 5 psi | 3 | 8 |
| P-10 | Wash Water Feed Pump - 825 gpm, 15 psi, 10 hp, CS | 4 | 13 |
| P-11 | Leach Filtrate Pump - 500 gpm, 5 psi, 1.5 hp, SS | as F-3 |  |
| P-12 | Wash Filtrate Pump - 250 gpm, 10 psi, 2 hp, SS | as F-3 |  |
| P-13 | Contactor Slurry Pump - 1000 gpm, 15 psi, 15 hp, SS | 6 | 17 |
| P-14 | Filtrate Pump (2) - 350 gpm, 7.5 psi, 3 hp, SS | as F-4 |  |
| P-15 | Contactor Slurry Pump (2) - 550 gpm, 7.5 psi, 6 hp, CS | 3 | 11 |
| P-16 | Acetone Centrate Pump (2) - 450 gpm, 7.5 psi, 5 hp, CS | as CG-1 |  |
| P-17 | Acetone Return Pump (3) - 20 gpm, 0.5 hp, CS, 15 psi | as D-1 |  |
| P-18 | Scrubber Water Return Pump - 150 gpm, 10 psi, 2 hp, CS | 2 | 16 |

(Continued)

### TABLE 39. (Continued)

| | | $K FOB | $K Installed |
|---|---|---|---|
| P-19 | Acetone Condensate Pump - 1400 gpm, 15 hp, CS, 15 psi | 5 | 15 |
| P-20 | Wash Filtrate Pump (2) - 250 gpm, 7.5 psi, 2 hp, SS | as F-2 | |
| P-21 | Filter Feed Pump (2) - 550 gpm, 10 psi, 5 hp, SS | 4 | 13 |
| P-22 | Filtrate Pump (2) - 250 gpm, 7.5 psi, 2 hp, SS | as F-5 | |
| P-23 | Wash Filtrate Pump (2) - 250 gpm, 7.5 psi, 2 hp, SS | as F-5 | |
| R-1 | Reactor - 23' ϕ x 115', CS with acid-brick lining, 45 psig | 808 | 1975 |
| R-2 | Regenerator - 10.5' ϕ x 63', 50 psig, CS with acid-brick lining | 219 | 534 |
| RV-1 | Rotary Valve (2) - 1 hp, 24" x 24", 20 RPM | 39 | 43 |
| RV-2 | Rotary Valve (3) - 0.5 hp, 18" x 18", 20 RPM | 25 | 27 |
| RV-3 | Rotary Valve (3) - 0.5 hp, 18" x 18", 20 RPM | 25 | 27 |
| S-1 | Separator - 0.5 hr Residence Time | 855 | 1710 |
| SS-1 | Acetone Stripper - 13' ϕ x 65', SS, 20 Trays, 15 psig | 192 | 327 |
| T-1 | Mix Tank (2) - 21' ϕ x 41', SS, 0 psig, 102,000 gal | 288 | 504 |
| T-2 | Knock-Out Drum (2) - 3200 gal, SS, 0 psig | 38 | 87 |
| T-3 | Flash Drum - 6100 gal, 7' ϕ x 21', SS, 2 psig | 40 | 91 |
| T-4 | Knock-Out Drum - 13500 gal, 8' ϕ x 24', SS, 0 psig | 42 | 81 |
| T-5 | Wash Filtrate Receiver (2) - 1600 gal., Vac, SS | as F-1 | |

(Continued)

TABLE 39. (Continued)

| | | $K<br>FOB | $K<br>Installed |
|---|---|---|---|
| T-6 | Contactor (2) - 25,000 gal, 0 psig, SS | 130 | 260 |
| T-7 | Filtrate Receiver (2) - 1600 gal, Vac, SS | as F-2 | |
| T-8 | Wash Water Hold Tank - 72,000 gal, 0 psig, FRP | 50 | 100 |
| T-9 | Filtrate Receiver - 2000 gal, Vac, SS | as F-3 | |
| T-10 | Wash Filtrate Receiver - 2500 gal, Vac, SS | as F-3 | |
| T-11 | Contactor - 40,000 gal, 0 psi, SS | 81 | 185 |
| T-12 | Filtrate Receiver (2) - 1300 gal, Vac, SS | as F-4 | |
| T-13 | Contactor (2) - 20,000 gal, 0 psig, CS | 33 | 66 |
| T-14 | Centrate Receiver (2) - 1300 gal, Vac, CS | as CG-1 | |
| T-15 | Dryer Condensate Receiver (3) - 140 gal, CS, 0 psig | as D-1 | |
| T-16 | Stripper Condensate Receiver - 9500 gal, CS, 15 psig | 9 | 17 |
| T-17 | Stripper Bottoms Separator - 2700 gal, Hastelloy C, 15 psig | 19 | 43 |
| T-18 | Acid Neutralizer Tank - 11,000 gal, FRP, 0 psig | 7 | 15 |
| T-19 | Filtrate Receiver (2) - 3000 gal, Vac, SS | as F-1 | |
| T-20 | Carbon Adsorption Drum - 5' ϕ x 10', FRP, 0 psig | 3 | 10 |
| T-21 | Wash Filtrate Receiver (2) - 1600 gal, Vac, SS | as F-2 | |
| T-22 | Contactor (2) - 25,000 gal, 0 psig, SS | 130 | 260 |
| T-23 | Filtrate Receiver (2) - 1600 gal, Vac, SS | as F-5 | |
| T-24 | Wash Filtrate Receiver - 1600 gal, Vac, SS | as F-5 | |

*CS/SS - Carbon Steel Sheet/Stainless Steel Tubes

TABLE 40. BATTERY LIMIT PROCESS COSTS – BASE CASE 1

| Capital Related Costs: | Annual Cost, $1000 |
|---|---|
| Depreciation - 10% straight line | 1,739 |
| Maintenance, insurance, taxes, interest - 15% of capital | 2,609 |
| Labor: | |
| Labor, 13 operating positions at $160,000/position | 2,080 |
| Utilities: | |
| Electric power, 2850 Kw at 5¢/Kw-hr | 1,128 |
| Cooling water, 16,700 gpm, 30°F rise at 5¢/1000 gal | 428 |
| Process water, 216 gpm, at 25¢/1000 gal | 26 |
| Heating, 321 MM Btu/hr, fired duty, 12.3 TPH coal product equivalent | - |
| Materials: | |
| Oxygen, 2.4 TPH at $50/ton | 940 |
| Nitrogen, 0.25 TPH (included in oxygen cost) | - |
| Sulfuric acid, 1.4 TPH at $55/ton | 615 |
| Lime, 2.6 TPH at $35/ton | 728 |
| Acetone, 0.1 TPH at $320/ton | 253 |
| Waste disposal, 9 TPH at $6/ton | 428 |
| TOTAL COST | 10,974 |

### 8.2.1.3 Process Economics--

The equipment list (Table 39) presented earlier shows that a 225 TPH battery limit Gravichem process train has an installed cost estimated to be 17.4 million dollars. That battery limit plant when incorporated with its associated off-sites represents an integrated grass roots coal desulfurization facility. The off-sites for a plant of this type are estimated to be approximately 50% of the installed battery limits cost(14) or in this case 8.7 million dollars.

The results of the integrated grass roots Gravichem process economic evaluation are presented in Table 41. Calculations were performed using three assumed run-of-mine (ROM) coal costs; \$15, \$20 and \$30 per ton. These values were selected since they represent the broad range of currently reported ROM coal costs (\$15/ton at mine mouth to \$30/ton reported delivery price at some plant sites).

As may be determined from the data (Table 41), the required market value of the treated coal product ranges from \$1.01/MM Btu with \$15/ton ROM feed coal to \$1.66/MM Btu with \$30/ton ROM feed material. An equivalent upgrading cost is found by deducting the cost of the ROM "dirty" coal energy (\$0.58/MM Btu, \$0.78/MM Btu, and \$1.16/MM Btu at \$15, \$20 and \$30/ton ROM coal respectively). The upgrading costs ranged from \$0.43/MM Btu to \$0.50/MM Btu when ROM coal feed varied from \$15/ton to \$30/ton.

### 8.2.2 Base Case 2 — TVA Kentucky No. 9 Coal

Base Case 2 involves the desulfurization of TVA Kentucky No. 9 coal via the Gravichem Process. The conceptual design described is based on a coal feed rate of 200 TPH for TVA coal from Hopkins County, Kentucky Number 9 seam, with a heating value of 12,400 Btu/lb. The coal contains 4.3% w/w total sulfur with a pyritic sulfur level of 2.4% w/w. Process flow diagrams (Dwg. Nos. 2473-5 and 6) for the design are presented as Figures 36a and 36b. The flow diagrams indicate equipment, key process temperatures and pressures, flow rates and compositions of key coal streams, and steam and raw material flow rates.

#### 8.2.2.1 Process Description--

Feed and mixer. 200 TPH (dry basis) coal are fed to the mixer T-1 from the feed hopper A-1 by conveyor C-1 after heating to 215$^{o}$F on the conveyor by flash steam and low pressure process steam. At the mixer the coal is contacted with recycled leach solution at 215$^{o}$F where the 0.75-hour residence time, in three stages, provides thorough wetting of the coal and partial reaction of the pyrite. The feed coal contains 10% moisture and 2.4% w/w pyritic sulfur on a dry basis.

Separator. The mixer slurry containing 24% coal is pumped to the separator S-1 through the slurry cooler E-1 where it is cooled to 176$^{o}$F. The

## TABLE 41. BASE CASE 1 — PROCESS ECONOMICS*

Annual Product, 1.66 MM Tons/yr
Energy Value, 43.4 x $10^6$ MM Btu/yr

| | ROM Coal Cost | | |
|---|---|---|---|
| Capital Related Requirements, $MM | $15/Ton | $20/Ton | $30/Ton |
| Battery Limit Capital | 17.39 | 17.39 | 17.39 |
| Off-site Capital | 8.70 | 8.70 | 8.70 |
| Overhead and Profit | 5.74 | 5.74 | 5.74 |
| Engineering and Design | 2.61 | 2.61 | 2.61 |
| Contingency | 5.17 | 5.17 | 5.17 |
| Total Plant Investment** | 39.61 | 39.61 | 39.61 |
| Interest for Construction | 6.68 | 6.68 | 6.68 |
| Start-up Costs | 7.40 | 9.18 | 12.74 |
| Working Capital (Utility Financing) | 7.04 | 9.05 | 13.07 |
| Total Capital Related Costs (Utility) | 60.73 | 64.52 | 72.10 |
| Operating Costs, $MM/Yr | | | |
| Raw Material (Coal) | 26.70 | 35.60 | 53.40 |
| Chemicals (Lime, Sulfuric Acid, Acetone) | 1.60 | 1.60 | 1.60 |
| Supplies | 0.88 | 0.88 | 0.88 |
| Disposal | 0.43 | 0.43 | 0.43 |
| Utilities | 3.09 | 3.09 | 3.09 |
| Labor (19 Positions) | 2.83 | 2.83 | 2.83 |
| Taxes and Insurance | 1.47 | 1.47 | 1.47 |
| Total Operating Costs | 37.00 | 45.90 | 63.70 |
| Required Coal Market Price, $/MM Btu | | | |
| Utility Financing | 1.01 | 1.22 | 1.66 |
| Upgrading Cost, $/MM Btu | | | |
| Utility Financing | 0.43 | 0.44 | 0.50 |

*Assumes, debt/equity = 75/25, interest on debt = 9%, return on equity = 15%.

**Equivalent to a plant capital investment of $68/kw.

separator is sized for one-hour residence time where the heavier high pyrite coal is separated as the sink fraction in the 1.3 specific gravity leach solution and the light low pyrite coal goes to the float fraction. 50% of the coal separates as the sink portion in a slurry containing 33% w/w coal based on current float/sink studies using TVA coal (Section 7). The sink slurry is pumped to the reactor R-1 for pyrite removal via the leach reaction. The float coal slurry, containing about 20% w/w coal, meets the total sulfur specification without further pyrite removal after washing and dewatering.

Float coal washing and dewatering. The 100 TPH coal in the float slurry is fed to a 3-stage countercurrent arrangement of three filters (F-1, F-2 and F-5) and two contactors (T-6 and T-22) where the leach solution is separated from the coal and the coal water washed such that the residual sulfate salts on the coal cake are less than 0.01% w/w sulfate sulfur. The coal cake from the last filtration stage, containing 33% moisture and 2.56% w/w total sulfur with a heating value of 13,830 Btu/lb, is well below the product specification of 4.0 lb $SO_2$/MM Btu.

Primary reactor. The 100 TPH coal in the sink slurry, containing 3.13% w/w pyritic sulfur, is pumped to the primary reactor R-1 where pyrite removal by the leach reaction takes place at 250°F and 35 psig. Based on bench-scale and RTU experimentation (Sections 6 and 7) the reactor is sized for six-hour residence time where the pyritic sulfur is reduced to a level of 0.53% w/w (dry basis). Simultaneous regeneration of the leach solution to maintain the ratio of $Fe^{+3}$ to total iron at 0.95 is accomplished by the injection of 3.9 TPH oxygen. The inert gas leaving the reactor contacts the recycled leach solution in the knockout drum T-4 prior to venting to the atmosphere. The heats of reaction and regeneration are removed in a pump-around loop where the reactor slurry is exchanged with cold recycle leach solution in exchanger E-4, maintaining the reactor temperature at 250°F.

Sink coal filtration and washing. The reactor slurry is cooled to 215°F by flashing to about 1 psig then pumped to a rotary drum vacuum filter F-3 where the leach solution is separated for recycle and the coal cake washed for the removal of sulfate salts. Wash water is provided from condensate of low pressure steam and recycled pond water. The coal cake from F-3 contains 33% w/w moisture.

Leach solution recycle loop. The leach solution filtrate stream from both the float and sink coal filters are recycled to the mixer T-1. The wash filtrates from F-1 and F-3 are dilute in iron sulfates and must be dewatered in the evaporator EV-1. A portion of the F-3 wash stream is pumped to the neutralizer in order to remove from the system the excess iron produced in the leach reaction. The feed to the evaporator is preheated to 264°F by the feed/bottoms exchanger E-3 and the evaporator feed preheater E-9. The evaporator is operated at 35 psig and 290°F such that the steam produced can be utilized for process heating service and the condensate recycled as filter wash water. The evaporator bottoms are concentrated in salt to the extent that the total leach solution recycle stream at the mixer T-1 is 7.5% w/w iron. The F-1 filtrate stream is heated to 237°F in exchangers E-4 and E-2 and fed to the regenerator R-2, operating at 35 psig and 250°F, where 0.5-hour residence time is provided to regenerate the leach solution to the extent that the combined recycle streams have a ratio of $Fe^{+3}$ to total iron equal to 0.90 at the mixer T-1. The oxygen requirement for regeneration is 0.92 TPH. The evaporator bottoms, regenerator effluent, F-3 filtrate and 2.8 TPH makeup sulfuric acid are combined and fed to the knockout drum T-4, then pumped to the mixer T-1 through knockout drum T-2 thus completing the recycle loop.

Acetone washing and elemental sulfur removal. The sink coal cake from filter F-3 is fed to the contactor T-11 where it is slurried with acetone to dissolve the elemental sulfur produced in the leach reaction. The resulting 40% coal slurry is then filtered on a rotary pan filter F-4 where the cake is washed with acetone. The elemental sulfur on the coal cake is reduced to about 0.2% w/w based on bench-scale studies (Section 7) and the sulfate sulfur further reduced to about 0.02% w/w. The acetone contacting equipment are vented to the atmosphere through a water scrubber GS-1 and a carbon bed T-20 for removal of acetone vapors.

Acetone recovery and sulfur removal. The acetone-water filtrate from filter F-4 containing elemental sulfur and sulfate salts are fed to the acetone stripper SS-1 operating at 250°F and 15 psig. The stripper bottoms consisting of water, molten elemental sulfur and sulfate salts are fed to the bottoms separator where the molten sulfur is removed and the water phase decanted. The sulfate laden water phase is cooled by E-12 and fed to the neutralizer. The stripper overhead vapor containing essentially all of the acetone feed is condensed and recycled to the contactor T-11.

Lime neutralization. The bottoms stream from the acetone stripper and a portion of the F-3 wash filtrate are removed from the system at the neutralizer in order to maintain the iron concentration in the leach solution at balance. The neutralizer feed streams are contacted with lime forming gypsum and iron oxides and pumped to the settling pond for solids removal. The solids-free pond water is treated and recycled to the system as wash water for the filters.

Coal drying. The acetone wet coal cake from filter F-4 containing about 27% acetone is fed to the coal drier F-1 where the coal is heated to 225°F and the acetone flashed by a 400°F stream of nitrogen gas. The acetone is condensed from the gas stream, which is a closed loop, and returned to the system for cake washing. The gas stream is compressed and reheated to 400°F by blower B-1 and recycle gas heaters E-7 and E-8. The dried coal cake is discharged from the drier and recombined with the float coal cake. The dried sink coal portion contains 2.5% w/w total sulfur and has a heating value of 11,990 Btu/lb. The combined coal product contains 2.53% total sulfur with a heating value of 12,930 Btu/lb resulting in a coal with 3.91 lb $SO_2$/MM Btu.

### 8.2.2.2 Battery Limit Process Costs--

Equipment list. The previous section of this document presented a conceptual process design and flow diagram (Figures 36a and 36b) for a battery limits processing facility treating 200 TPH of feed coal (193.3 TPH of desulfurized coal product). The process was designed to reduce the 4.3% w/w total sulfur feed coal to a combined Gravichem product containing no more than 4.0 lbs $SO_2$/MM Btu. An equipment list, tabulating the required major equipment, is presented as Table 42. The total battery limits FOB equipment cost was determined to be 8.7 million dollars while the total installed equipment cost is 15.3 million dollars.

Battery limits process operating costs. The total estimated battery limit processing cost is presented in Table 43. As may be determined from Table 43, the estimated total annualized operating cost results in an equivalent battery limit production cost of $8.63/ton of coal product. This production cost is based on cleaned coal production 185.5 TPH (193.3 TPH of desulfurized product

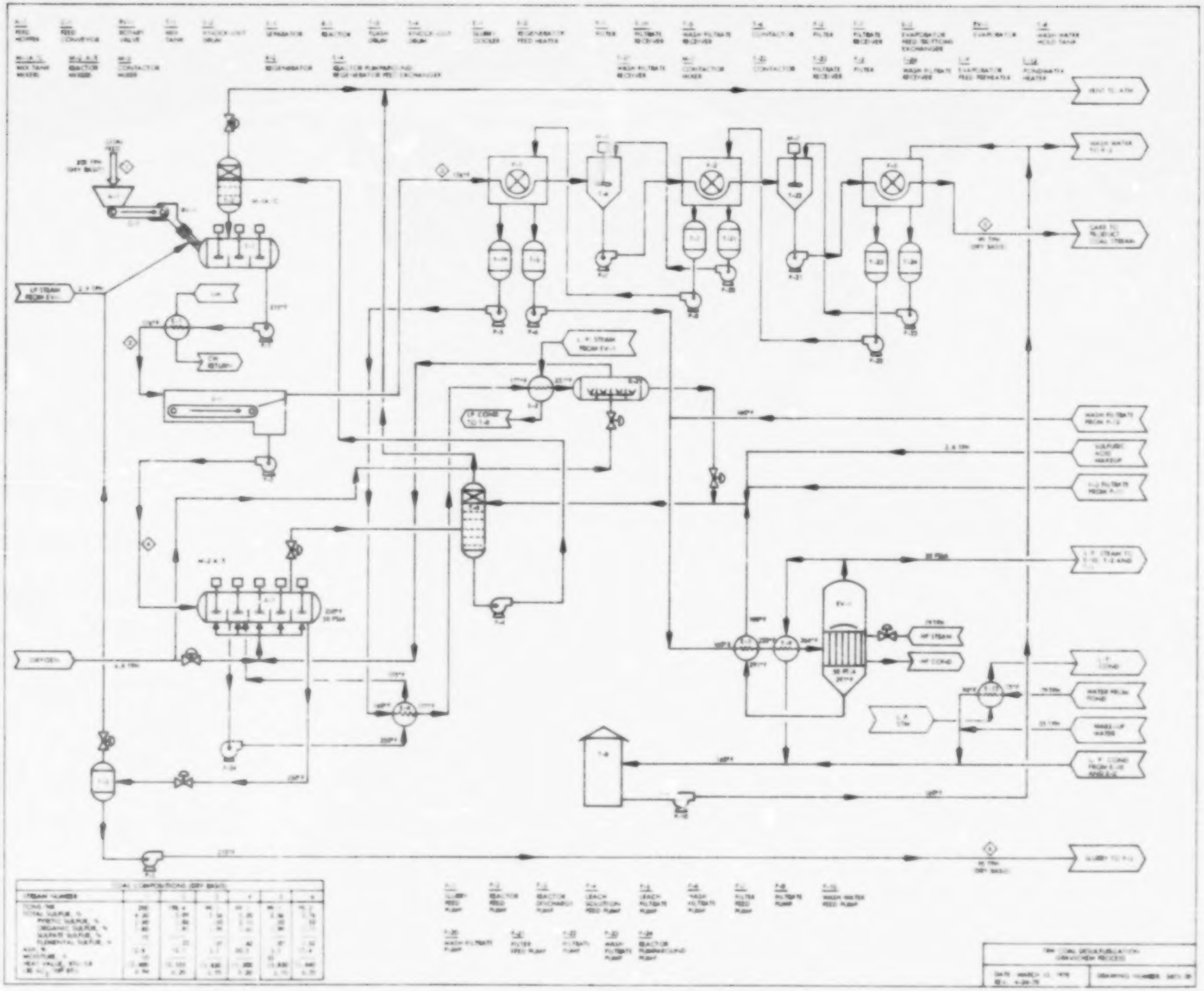

VENT TO ATM
WASH WATER
CAKE TO REJECT COAL STREAM
SULFURIC ACID MAKEUP
L.P. COND
WATER FROM POND
MAKE-UP WATER
OXYGEN
LP STEAM FROM EV-1
CW
CW RETURN
L.P. STEAM FROM EV-1
LP COND

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Figure 36a. TRW Coal Desulfurization Gravichem Process

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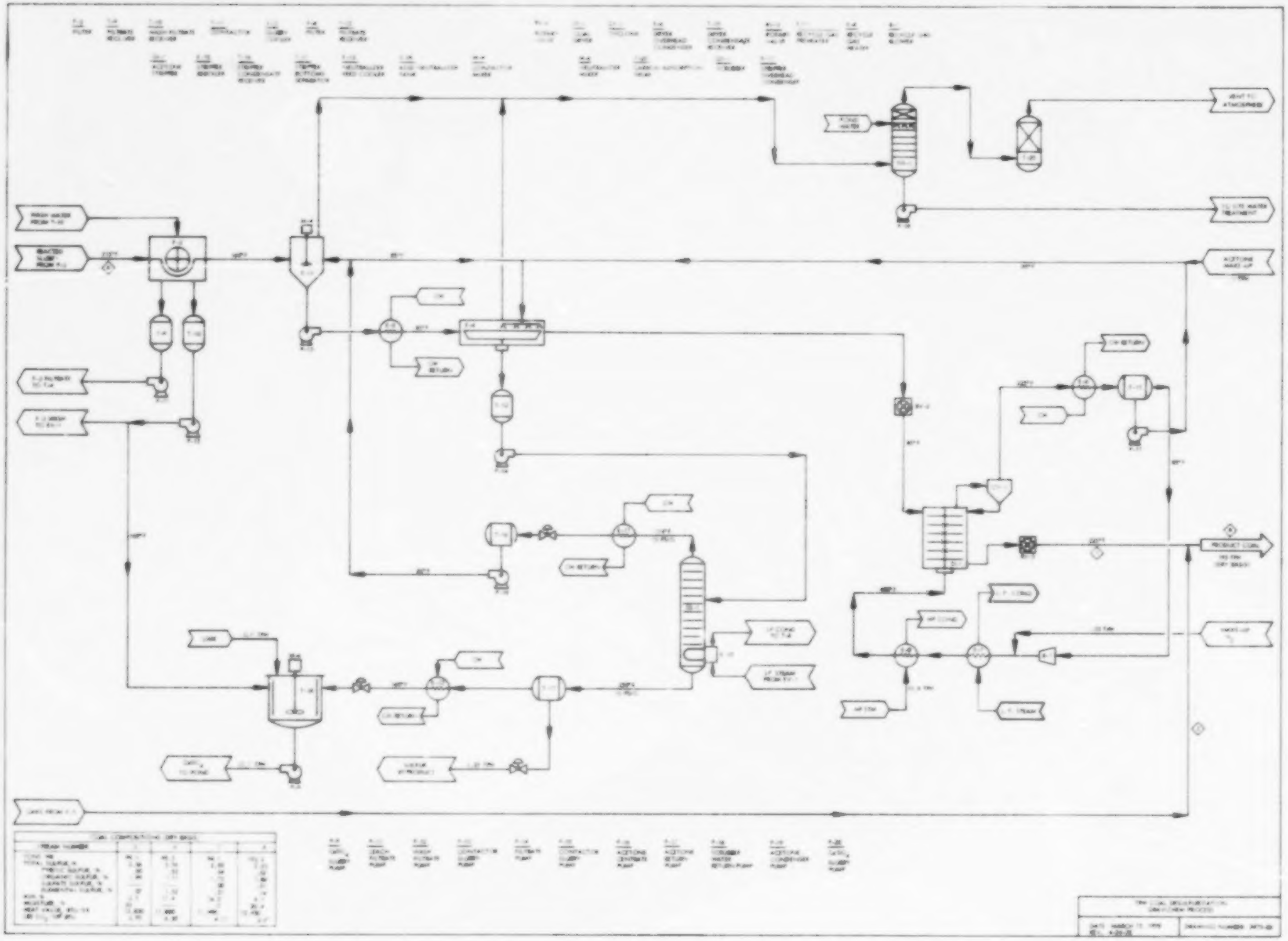
VENT TO ATMOSPHERE
TO SITE WATER TREATMENT
ACETONE MAKE UP
PRODUCT COAL
MAKE UP

Figure 36b. TRW Coal Desulfurization Gravichem Process

## TABLE 42. BASE CASE 2 — PROCESS EQUIPMENT LIST

| MAJOR PROCESS EQUIPMENT $8.67 MM FOB, $15.31 MM INSTALLED | | $K FOB | $K Installed |
|---|---|---|---|
| A-1 | Feed Hopper - 10,000 ft$^3$ | 22 | 26 |
| B-1 | Recycle Gas Blower (3) - CS, 1.7 Compression Ratio, 85 hp | as D-1 | |
| C-1 | Feed Conveyor - 40 in. wide x 20 ft x 10 hp, 200 ft/min. | 16 | 27 |
| CY-1 | Cyclone (3) - 5 psig, 850 ft$^3$, CS | as D-1 | |
| D-1 | Coal Dryer (3) - 30' $\phi$ 55', CS, 5 psig, 15 hp, 54 trays, 60 min. | 2450 | 3062 |
| E-1 | Slurry Cooler - 3185 ft$^2$, CS/SS | 76 | 205 |
| E-2 | Regenerator Feed Heater - 1040 ft$^2$, CS/Hastelloy C | 37 | 102 |
| E-3 | Evaporator Feed/Bottoms Exchanger - 2890 ft$^2$, Hastelloy C/Hastelloy C | 95 | 258 |
| E-4 | Reactor Pumparound/Regenerator Feed Exchanger - 1360 ft$^2$, Hastelloy C/Hastelloy C | 65 | 177 |
| E-5 | Slurry Cooler - 3400 ft$^2$, CS/SS | 78 | 212 |
| E-6 | Dryer Overhead Condenser (3) - 1770 ft$^2$, CS/CS | as D-1 | |
| E-7 | Recycle Gas Preheater (3) - 1500 ft$^2$, CS/SS | as D-1 | |
| E-8 | Recycle Gas Heater (3) - 1050 ft$^2$, CS/CS | as D-1 | |
| E-9 | Evaporator Feed Preheater - 1140 ft$^2$, CS/Hastelloy C | 37 | 102 |
| E-10 | Stripper Reboiler - 3120 ft$^2$, Hastelloy C | 51 | 142 |
| E-11 | Stripper Overhead Condenser - 7421 ft$^2$, CS/CS | 114 | 362 |

(Continued)

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TABLE 42. (Continued)

| | | $K FOB | $K Installed |
|---|---|---|---|
| E-12 | Neutralizer Feed Cooler - 800 ft$^2$, CS/SS | 31 | 90 |
| E-13 | Pondwater Heater - 50 ft$^2$, CS/SS | 8 | 25 |
| EV-1 | Evaporator - 1400 ft$^2$, 35 psig, CS with titanium clad | 722 | 1155 |
| F-1 | Rotary Drum Vacuum Filter Package - 12' ϕ x 24', 912 ft$^2$, SS, 250 hp (inc. vac. sys.) | 184 | 292 |
| F-2 | Rotary Drum Vacuum Filter Package - 12' ϕ x 24', 912 ft$^2$, SS, 250 hp (inc. vac. sys.) | 184 | 292 |
| F-3 | Rotary Drum Vacuum Filter Package - 12' ϕ x 24', 912 ft$^2$, SS, 250 hp (inc. vac. sys.) | 184 | 292 |
| F-4 | Rotary Pan Filter Package (2) - 24' ϕ, 445 ft$^2$, SS, 105 hp (inc. vac. sys.) | 941 | 1491 |
| F-5 | Rotary Drum Vacuum Filter Package - 12' ϕ x 24', 912 ft$^2$, SS, 250 hp (inc. vac. sys.) | 184 | 292 |
| GS-1 | Scrubber - 5' ϕ x 30', 20 trays, 0 psig, CS | 13 | 21 |
| M-1 A/C | Mix Tank Mixers (6) - 25 hp, SS | 57 | 92 |
| M-2 A/E | Reactor Mixers (5) - 190 hp, Hastelloy C | 194 | 315 |
| M-3 | Contactor Mixer - 50 hp, SS | 13 | 21 |
| M-4 | Contactor Mixer - 50 hp, SS | 13 | 21 |
| M-6 | Neutralizer Mixer - 15 hp, SS | 7 | 11 |
| M-7 | Contactor Mixer - 50 hp, SS | 13 | 21 |

(Continued)

TABLE 42. (Continued)

| | | $K<br>FOB | $K<br>Installed |
|---|---|---|---|
| P-1 | Slurry Feed Pump (2) - 1350 gpm, 15 psi, 15 hp, SS | 15 | 45 |
| P-2 | Reactor Feed Pump - 1000 gpm, 15 psi, 10 hp, SS | 5 | 15 |
| P-3 | Reactor Discharge Pump - 960 gpm, 15 psi, 10 hp, SS | 5 | 15 |
| P-4 | Leach Solution Feed Pump (2) - 960 gpm, 15 psi, 15 hp, SS | 8 | 21 |
| P-5 | Leach Filtrate Pump - 1120 gpm, 75 psi, 75 hp, SS | as F-1 | |
| P-6 | Wash Filtrate Pump - 400 gpm, 70 psi, 20 hp, SS | as F-1 | |
| P-7 | Filter Feed Pump - 850 gpm, 10 psi, 7.5 hp, SS | 5 | 18 |
| P-8 | Filtrate Pump - 340 gpm, 7.5 psi, 3 hp, SS | as F-2 | |
| P-9 | $CaSO_4$ Slurry Pump - 320 gpm, 2 hp, SS, 5 psi | 3 | 8 |
| P-10 | Wash Water Feed Pump - 730 gpm, 15 psi, 10 hp, CS | 4 | 13 |
| P-11 | Leach Filtrate Pump - 500 gpm, 5 psi, 1.5 hp, SS | as F-3 | |
| P-12 | Wash Filtrate Pump - 250 gpm, 10 psi, 2 hp, SS | as F-3 | |
| P-13 | Contactor Slurry Pump - 1000 gpm, 15 psi, 15 hp, SS | 6 | 17 |
| P-14 | Filtrate Pump (2) - 350 gpm, 7.5 psi, 3 hp, SS | as F-4 | |
| P-17 | Acetone Return Pump (3) - 65 gpm, 1.5 hp, CS, 15 psi | as D-1 | |
| P-18 | Scrubber Water Return Pump - 150 gpm, 10 psi, 2 hp, CS | 2 | 16 |
| P-19 | Acetone Condensate Pump - 540 gpm, 7.5 hp, CS, 15 psi | 3 | 9 |

(Continued)

TABLE 42. (Continued)

| | | $K<br>FOB | $K<br>Installed |
|---|---|---|---|
| P-20 | Wash Filtrate Pump - 370 gpm, 7.5 psi, 5 hp, SS | as F-2 | |
| P-21 | Filter Feed Pump - 850 gpm, 10 psi, 7.5 hp, SS | 5 | 18 |
| P-22 | Filtrate Pump - 340 gpm, 7.5 psi, 3 hp, SS | as F-5 | |
| P-23 | Wash Filtrate Pump - 370 gpm, 7.5 psi, 5 hp, SS | as F-5 | |
| P-24 | Reactor Pumparound Pump - 325 gpm, 15 psi, 5 hp, Hastelloy C | 4 | 12 |
| R-1 | Reactor - 23' $\phi$ x 115', CS with acid-brick lining, 45 psig | 808 | 1975 |
| R-2 | Regenerator - 10' $\phi$ x 61', 50 psig, CS with acid-brick lining | 219 | 534 |
| RV-1 | Rotary Valve (2) - 1 hp, 24" x 24", 20 RPM | 39 | 43 |
| RV-2 | Rotary Valve (3) - 0.5 hp, 18" x 18", 20 RPM | 25 | 27 |
| RV-3 | Rotary Valve (3) - 0.5 hp, 18" x 18", 20 RPM | 25 | 27 |
| S-1 | Separator - 0.5 hr Residence Time (Acid Brick) | 855 | 1710 |
| SS-1 | Acetone Stripper - 8' $\phi$ x 54', SS, 20 Trays, 15 psig | 139 | 236 |
| T-1 | Mix Tank (2) - 20' $\phi$ x 40', SS, 0 psig, 91,330 gal | 274 | 480 |
| T-2 | Knock-Out Drum (2) - 3200 gal, SS, 0 psig | 38 | 87 |
| T-3 | Flash Drum - 6100 gal, 7' $\phi$ x 21', SS, 2 psig | 40 | 91 |
| T-4 | Knock-Out Drum - 13,500 gal, 8' $\phi$ x 24', SS, 0 psig | 42 | 81 |
| T-5 | Wash Filtrate Receiver - 2000 gal, Vac, SS | as F-1 | |
| T-6 | Contactor - 40,000 gal, 0 psig, SS | 81 | 185 |

(Continued)

TABLE 42. (Continued)

| | | $K FOB | $K Installed |
|---|---|---|---|
| T-7 | Filtrate Receiver - 2000 gal, Vac, SS | as F-2 | |
| T-8 | Wash Water Hold Tank - 40,000 gal, 0 psig, FRP | 34 | 67 |
| T-9 | Filtrate Receiver - 2000 gal, Vac, SS | as F-3 | |
| T-10 | Wash Filtrate Receiver - 2500 gal, Vac, SS | as F-3 | |
| T-11 | Contactor - 40,000 gal, 0 psig, SS | 81 | 185 |
| T-12 | Filtrate Receiver (2) - 1300 gal, Vac, SS | as F-4 | |
| T-15 | Dryer Condensate Receiver (3) - 450 gal, CS, 0 psig | as D-1 | |
| T-16 | Stripper Condensate Receiver - 3400 gal, CS, 15 psig | 5 | 9 |
| T-17 | Stripper Bottoms Separator - 2700 gal, Hastelloy C, 15 psig | 19 | 43 |
| T-18 | Acid Neutralizer Tank - 15,000 gal, FRP, 0 psig | 9 | 19 |
| T-19 | Filtrate Receiver - 5500 gal, Vac, SS | as F-1 | |
| T-20 | Carbon Adsorption Drum - 5' ϕ x 10', FRP, 0 psig | 3 | 10 |
| T-21 | Wash Filtrate Receiver - 2500 gal, Vac, SS | as F-2 | |
| T-22 | Contactor - 40,000 gal, 0 psig, SS | 81 | 185 |
| T-23 | Filtrate Receiver- 2000 gal, Vac, SS | as F-5 | |
| T-24 | Wash Filtrate Receiver - 2500 gal, Vac, SS | as F-5 | |

---

*CS/SS - Carbon Steel Sheet/Stainless Steel Tubes

## TABLE 43. BATTERY LIMITS PROCESS COSTS - BASE CASE 2

| Capital Related Costs: | Annual Cost, $1000 |
|---|---|
| Depreciation - 10% straight line | 1,531 |
| Maintenance, insurance, taxes, interest - 15% of capital | 2,296 |
| Labor: | |
| Labor, 12 operating positions at $160,000/position | 1,920 |
| Utilities: | |
| Electric power, 2280 Kw at 5¢/Kw-hr | 902 |
| Cooling water, 11,500 gpm, 30°F rise at 5¢/1000 gal | 273 |
| Process water, 100 gpm at 25¢/1000 gal | 12 |
| Heating, 201 MM Btu/hr, fired duty, 7.8 TPH coal product equivalent | - |
| Materials: | |
| Oxygen, 4.8 TPH at $50/ton | 1,909 |
| Nitrogen, 0.53 TPH (included in oxygen cost) | - |
| Sulfuric acid, 2.7 TPH at $55/ton | 1,194 |
| Lime, 5.5 TPH at $35/ton | 1,530 |
| Acetone, 0.1 TPH at $320/ton | 253 |
| Waste disposal, 18 TPH at $6/ton | 846 |
| TOTAL COST | 12,666 |

less 7.8 TPH for process steam generation). The battery limit processing facility therefore operates with an overall coal yield of 93% on a dry weight basis and an overall energy yield of 97% on a Btu basis. The coal required for process and oxygen plant electric power consumption is 2.1 TPH resulting in a 95.6% net overall energy efficiency when included with the coal usage for plant steam generation. The noncapitalized battery limit operating cost, the total

process operating cost less the annual depreciation charge (10% of installed equipment), is \$7.03/ton of coal feed (28¢/MM Btu equivalent) or \$7.58/ton of coal product (29¢/MM Btu equivalent). This noncapitalized operating cost essentially represents a pure battery limit operating cost.

#### 8.2.2.3 Process Economics--

The Base Case 2 design, as discussed earlier, resulted in an installed battery limit plant costing 15.3 million dollars. Using rational presented in Section 8.2.1.3, it is therefore expected that the associated off-sites would cost an additional 7.7 million dollars. The resultant integrated grass roots facility economics are then determined to be as shown in Table 44.

As may be seen, the required market value of the coal product ranges from \$1.09/MM Btu with \$15/ton ROM feed coal to \$1.75/MM Btu with \$30/ton ROM feed material. The equivalent upgrading cost, found by deducting the cost of the ROM "dirty" coal energy (\$0.60/MM Btu, \$0.81/MM Btu, and \$1.21/MM Btu at \$15, \$20 and \$30/ton ROM coal respectively) from the required market value, ranges from \$0.49/MM Btu to \$0.54/MM Btu.

## 8.3 ENGINEERING ANALYSIS CONCLUSIONS

As discussed earlier, two conceptual full-scale process designs and cost estimates were generated based on the most current technical data available. Each of the two design packages, termed "Base Cases", were aimed at evaluating the recently conceived Gravichem Process as applied to two differing coals. Furthermore, each Base Case deals with desulfurizing coal to different residual sulfur levels. Base Case 1 is representative of Gravichem application to a relatively low sulfur coal (1.51% w/w total sulfur with 1.0% w/w pyritic sulfur) when processed to a residual total sulfur content equivalent to 1.2 lbs $SO_2$/MM Btu. Base Case 2 is typical of Gravichem application to a relatively high sulfur coal (4.3% w/w total sulfur with 2.4% w/w pyritic sulfur) when processed to the less stringent equivalent sulfur limit of 4 lbs $SO_2$/MM Btu.

### 8.3.1 Base Case Results

Table 45 presents a summary of the Gravichem process economics as they relate to processing low (Base Case 1) and high (Base Case 2) sulfur content coals. It should be noted that the economics picture, as presented, is specific

## TABLE 44. BASE CASE 2 — PROCESS ECONOMICS*

Annual Product, 1.46 MM Tons/yr
Energy Value, 38.0 x $10^6$ MM Btu/yr

| | ROM Coal Cost | | |
|---|---|---|---|
| Capital Related Requirements, $MM | $15/Ton | $20/Ton | $30/Ton |
| Battery Limit Capital | 15.31 | 15.31 | 15.31 |
| Off-site Capital | 7.66 | 7.66 | 7.66 |
| Overhead and Profit | 5.05 | 5.05 | 5.05 |
| Engineering and Design | 2.30 | 2.30 | 2.30 |
| Contingency | 4.55 | 4.55 | 4.55 |
| Total Plant Investment** | 34.87 | 34.87 | 34.87 |
| Interest for Construction | 5.88 | 5.88 | 5.88 |
| Start-up Costs | 7.08 | 8.66 | 11.83 |
| Working Capital (Utility Financing) | 6.35 | 8.13 | 11.71 |
| Total Capital Related Costs (Utility) | 54.18 | 57.54 | 64.29 |
| Operating Costs, $MM/Yr | | | |
| Raw Material (Coal) | 23.76 | 31.68 | 47.52 |
| Chemicals (Lime, Sulfuric Acid, Acetone) | 2.98 | 2.98 | 2.98 |
| Supplies | 0.79 | 0.79 | 0.79 |
| Disposal | 0.85 | 0.85 | 0.85 |
| Utilities | 3.10 | 3.10 | 3.10 |
| Labor (18 Positions) | 2.61 | 2.61 | 2.61 |
| Taxes and Insurance | 1.29 | 1.29 | 1.29 |
| Total Operating Costs | 35.38 | 43.30 | 59.14 |
| Required Coal Market Price, $/MM Btu | | | |
| Utility Financing | 1.09 | 1.31 | 1.75 |
| Upgrading Cost, $/MM Btu | | | |
| Utility Financing | 0.49 | 0.50 | 0.54 |

*Assumes, debt/equity = 75/25, interest on debt = 9%, return on equity = 15%.

**Equivalent to a plant capital investment of $69/kw.

TABLE 45. SUMMARY OF BASE CASE ECONOMICS RESULTS

| Cost | Base Case 1* -Martinka Coal- 225 TPH Coal Feed Basis | | | Base Case 2** -Kentucky No. 9 Coal- 200 TPH Coal Feed Basis | | | Adjusted Base Case 2*** -Kentucky No. 9 Coal- 225 TPH Coal Feed Basis | | |
|---|---|---|---|---|---|---|---|---|---|
| ROM Coal Cost $/Ton | 15 | 20 | 30 | 15 | 20 | 30 | 15 | 20 | 30 |
| Battery Limit Capital - $ MM | 17.4 | 17.4 | 17.4 | 15.3 | 15.3 | 15.3 | 17.2 | 17.2 | 17.2 |
| Total Plant Investment - $ MM | 39.6 | 39.6 | 39.6 | 34.9 | 34.9 | 34.9 | 39.2 | 39.2 | 39.2 |
| Total Operating Costs - $ MM/Yr | 37.0 | 45.9 | 63.7 | 35.4 | 43.3 | 59.1 | 39.8 | 48.7 | 66.5 |
| Required Product Market Price - $/MM Btu | 1.01 | 1.22 | 1.66 | 1.09 | 1.31 | 1.75 | 1.09 | 1.31 | 1.75 |
| Upgrading Cost $/MM Btu | .43 | .44 | .50 | .49 | .50 | .54 | .49 | .50 | .54 |

* Mine cleaned Martinka coal, 1.51% w/w total sulfur as fed, 1.2 lbs $SO_2$/MM Btu as processed, 1.66 MM TPY product, 43.4 X $10^6$ MM Btu/yr energy value.

** TVA supplied Kentucky No. 9 coal, 4.3% w/w total sulfur as fed, 4 lbs $SO_2$/MM Btu as processed, 1.46 MM TPY product, 38.0 X $10^6$ MM Btu/yr energy value.

*** Base Case 2 adjusted to an equivalent 1.64 MM TPY product, 42.8 X $10^6$ MM Btu/yr energy value.

to utility financing under the ground rules as detailed in Section 8.1.3.3. As may be seen from the table, the resultant upgrading costs range from \$0.43/MM Btu to \$0.50/MM Btu for the low sulfur coal case while the range is \$0.49/MM Btu to \$0.54/MM Btu for the higher sulfur Kentucky coal case. The low sulfur Base Case 1, which requires 0.79% w/w pyritic sulfur removal, has essentially the same capital requirement as Base Case 2 which effects a 1.88% w/w pyritic sulfur removal. This finding is substantiated when the Base Case 2 economics are adjusted to reflect comparable plant throughputs. The adjusted Base Case 2 economics are also presented on Table 45.

The apparent higher processing costs (upgrading cost) associated with Base Case 2 are generally the direct result of reacting and removing greater quantities of pyrite. The additional pyrite removal required by the Kentucky No. 9 coal (1.88% w/w as compared to 0.79% w/w for the Martinka coal) requires a directly proportional increase in certain operating costs. Specific costs which increased in Base Case 2 are associated with oxygen consumption as a regenerant, lime utilization for neutralization of sulfate, sulfuric acid makeup, and sulfur and gypsum disposal.

Bench-scale processing of Kentucky No. 9 sink (Section 7), performed during the latter stages of the design effort, indicate that ash other than pyrite is also leached from the coal during processing. The bench-scale data shows that the sink processed material will have an ash content ranging from 9.5% to 10.5% w/w while the process design material balance, which considers only pyrite removal, shows an ash content of 16.3% w/w. Incorporating this information into the overall process design and assuming a 10% ash content in the processed sink would result in a heating value of 12,890 Btu/lb for the sink coal. The combined float/sink product would therefore have an ash content of 6.5% w/w with a heating value of 13,390 Btu/lb. The net energy output of the plant would remain unchanged although processing costs would increase somewhat owing to increased neutralization and disposal costs for the removal of the additional ash. This new information would, however, indicate that a significantly cleaner (less ash) and therefore more desirable, desulfurized coal product would be generated than is indicated by the Base Case 2 process design.

### 8.3.2 Cost Sensitivity Analysis

In addition to each of the specific Base Case studies (Sections 8.2.1 and 8.2.2), a parametric analysis relating to process economics was performed to evaluate cost sensitivity. As part of the sensitivity study, three process cost related elements were varied. For each Base Case, installed battery limit capital cost was varied to evaluate the dependence of the bottom line upgrading cost on equipment cost estimates. The assumed battery limits cost was allowed to vary by approximately ±50% while all operating costs were held constant. Figures 37 and 38 present the effects of battery limit capital on upgrading costs as a function of ROM coal cost for each of the Base Cases. Figures 39 and 40 are cross plots showing the effects of ROM coal cost on upgrading cost as a function of battery limit capital. As may be seen from the Figures, upgrading costs can vary from approximately -9¢/MM Btu to +10¢/MM Btu over the range of ±50% of the Base Case battery limit capital for any given ROM coal cost. This holds true for both high and low sulfur coal processing.

Another variable evaluated was that of percent pyrite or pyritic sulfur removed. In this study, the feed coal for each Base Case was varied with respect to starting pyrite content. The resultant pyritic sulfur removal requirements were then determined in order to meet the appropriate residual sulfur levels for each of the cases. In this evaluation, the capital costs were assumed to remain constant and the appropriate operating costs (oxygen, lime, sulfuric acid, and disposal) were modified. The results of that evaluation are presented in Figures 41, 42, 43 and 44. Figures 41 and 42 present the upgrading costs for each case as a function of percent pyritic sulfur removed for each of the three ROM coal costs. Figures 43 and 44 indicate the upgrading costs as a function of ROM coal cost at several pyritic sulfur removal levels. The sulfur removal levels ranged from 0.5% w/w to 4% w/w for each case. As may be seen from the Figures, the resultant upgrading costs vary significantly with the amount of pyritic sulfur removed. In fact, over the range evaluated for both the high and low sulfur cases, the upgrading costs increase by 65% to 77% of the 0.5% w/w removal values as the amount of pyritic sulfur removed increases to 4% w/w.

The third variable evaluated was the percent float which is allowed to, in essence, bypass the conventional Meyers Process. For each Base Case, the float/sink ratio was allowed to vary from 33/66 to 66/33 (Base Case 1 is a 55/45 split while Base Case 2 is a 50/50 split). For this analysis, essentially all operating costs were held constant while the capital related costs

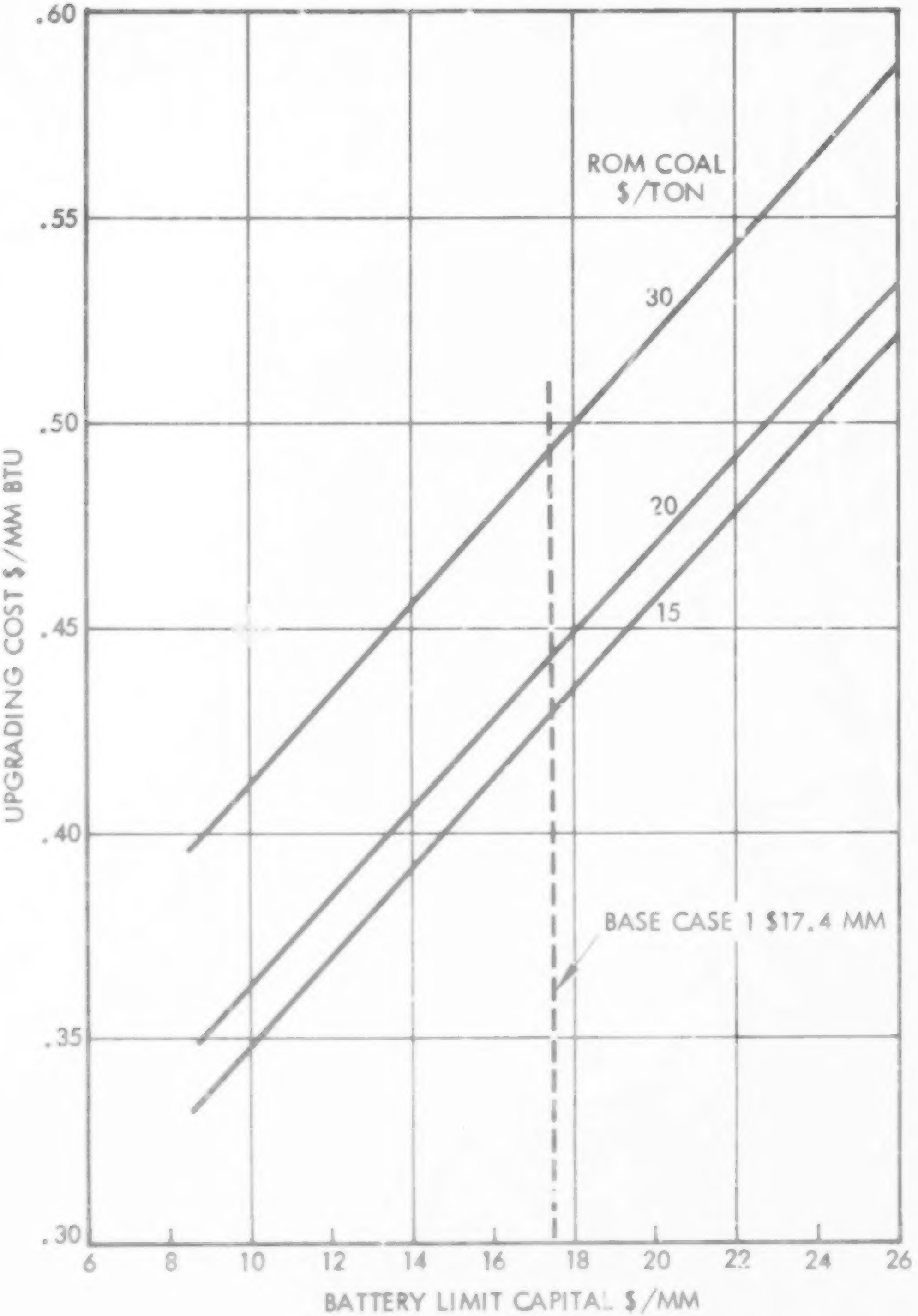

Figure 37. Base Case 1. Upgrading Cost vs. Battery Limit Capital

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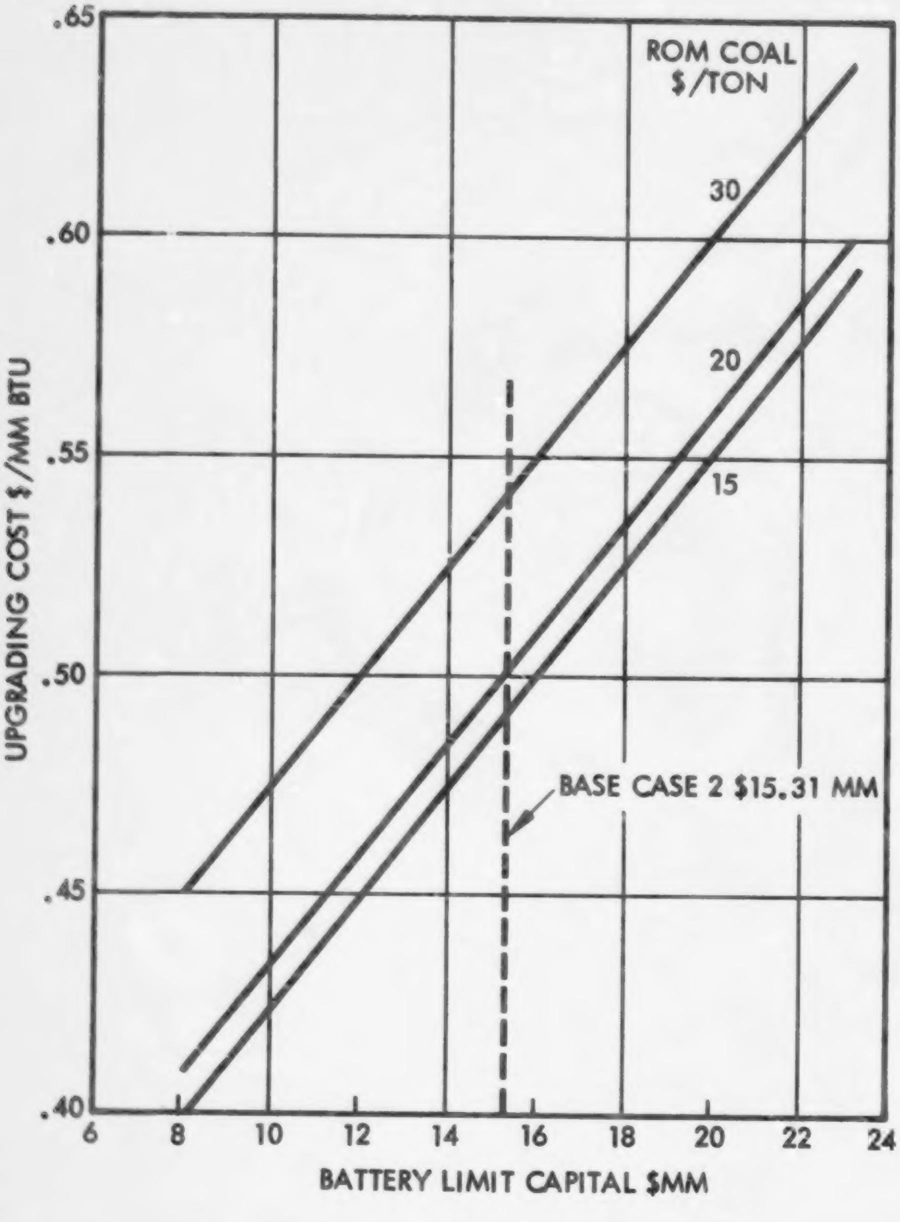

Figure 38. Base Case 2. Upgrading Cost vs. Battery Limit Capital

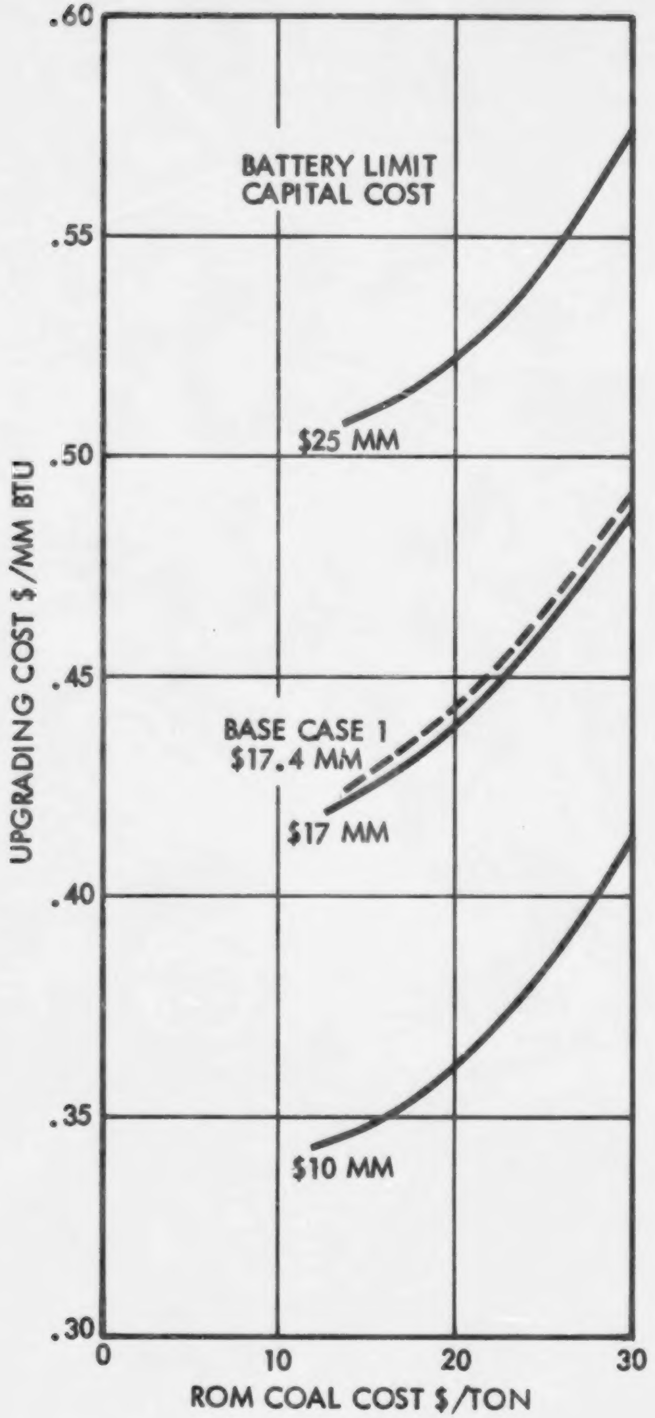

Figure 39. Base Case 1. Upgrading Cost vs. ROM Coal Cost

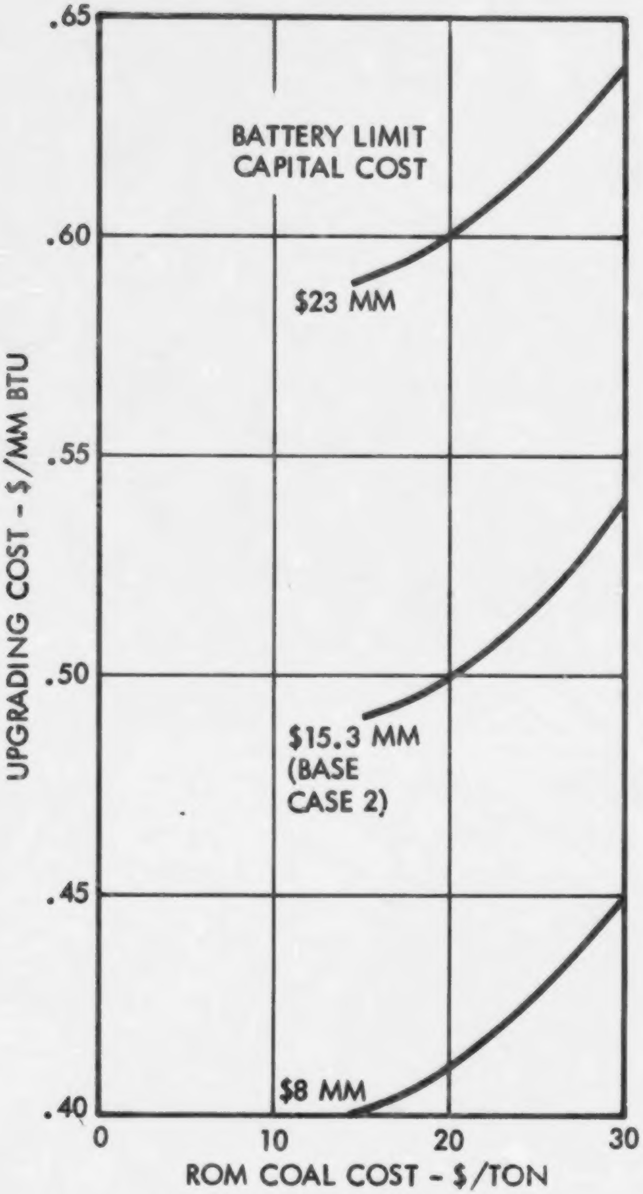

Figure 40. Base Case 2. Upgrading Cost vs. ROM Coal Cost

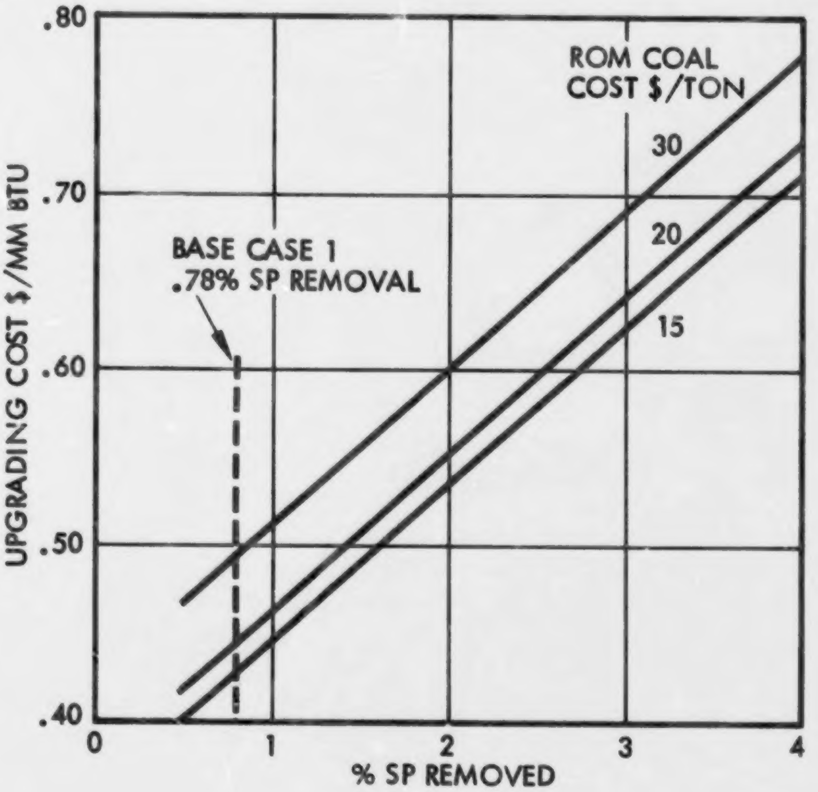

Figure 41. Base Case 1. Upgrading Cost vs. % Pyritic Sulfur Removed

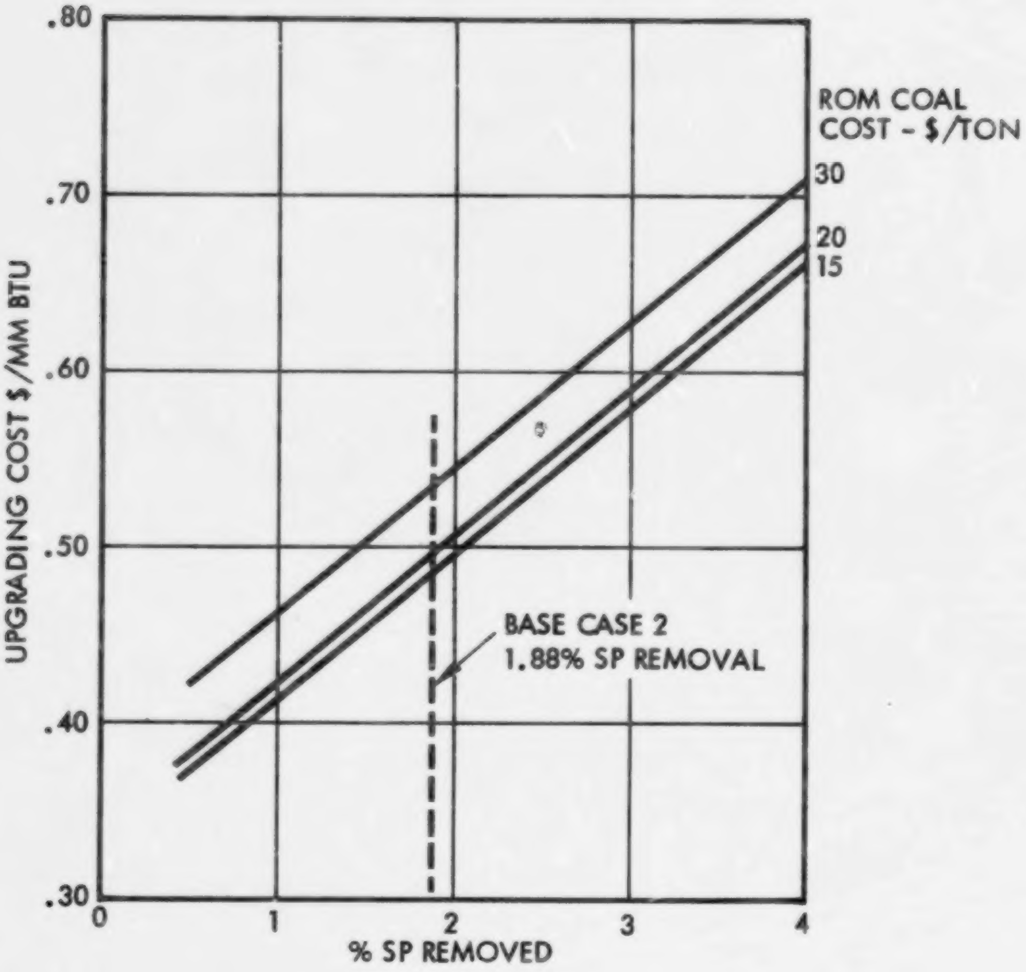

Figure 42. Base Case 2. Upgrading Cost vs. % Pyritic Sulfur Removed

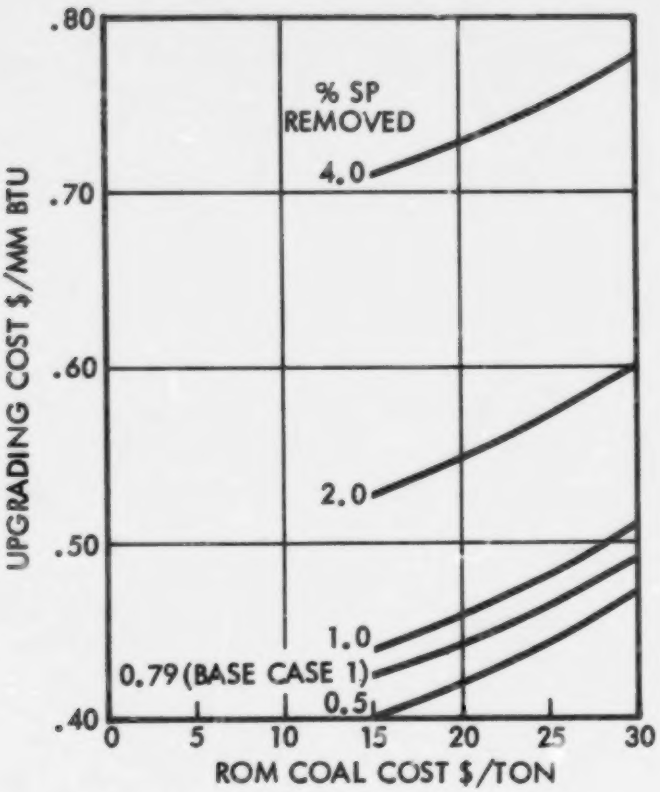

Figure 43. Base Case 1. Upgrading Cost vs. ROM Coal Cost at Different Levels of Pyritic Sulfur Removal

(i.e., battery limit costs, off-sites, etc.) were adjusted. The capital costs were adjusted to reflect the appropriate percent treatment in the more costly Meyers Process portion of the plant, and the less costly bypass float washing. In all cases, the costs associated with mixing, float/sink separation, and wash water generator (evaporator) were held constant.

Figures 45 and 46 show the effect of float processing on the upgrading costs as a function of ROM coal cost. Figures 47 and 48 present the cross plots indicating upgrading costs as a function of ROM coal costs at several float/sink ratios. As may be seen from the Figures, the overall processing costs do indeed drop with increasing float percentage. The costs drop by approximately 5¢/MM Btu over the float/sink ratio range of 0.5 to 2 (i.e., 33/66 to 66/33) for each of the ROM coal costs evaluated. This finding holds true for both the high and low sulfur coal base cases.

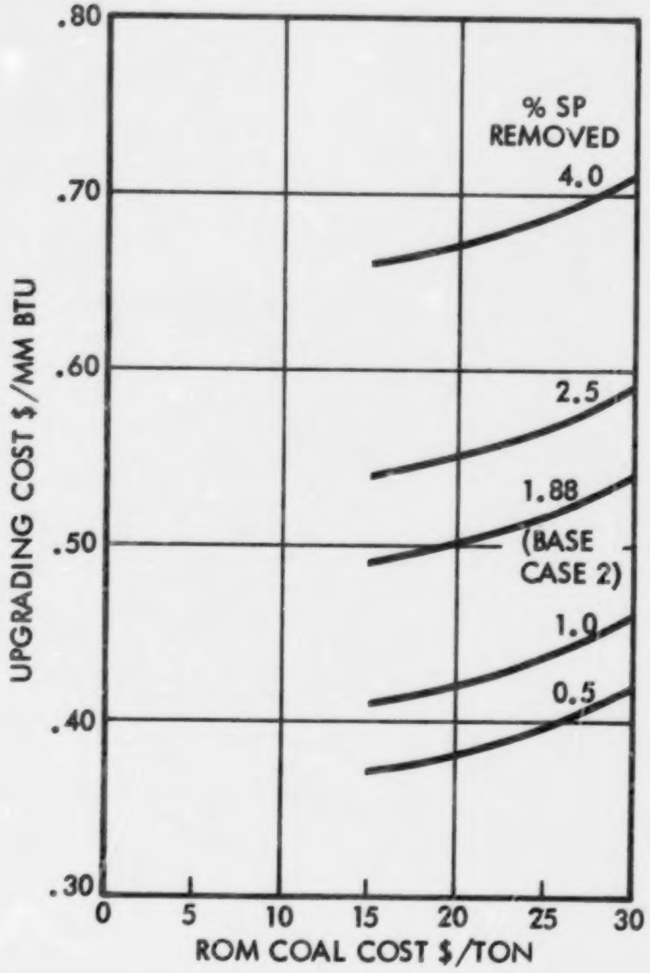

Figure 44. Base Case 2. Upgrading Cost vs. ROM Coal Cost at Different Levels of Pyritic Sulfur Removal

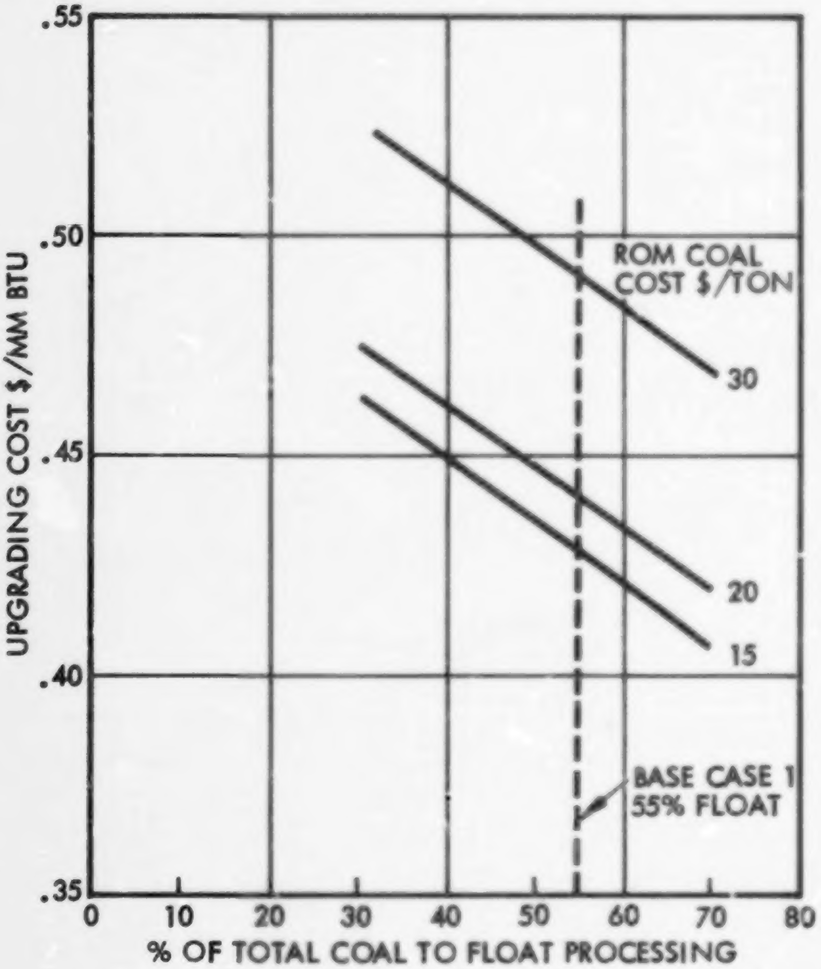

Figure 45. Base Case 1. Upgrading Cost vs. % of Total Coal to Float Processing

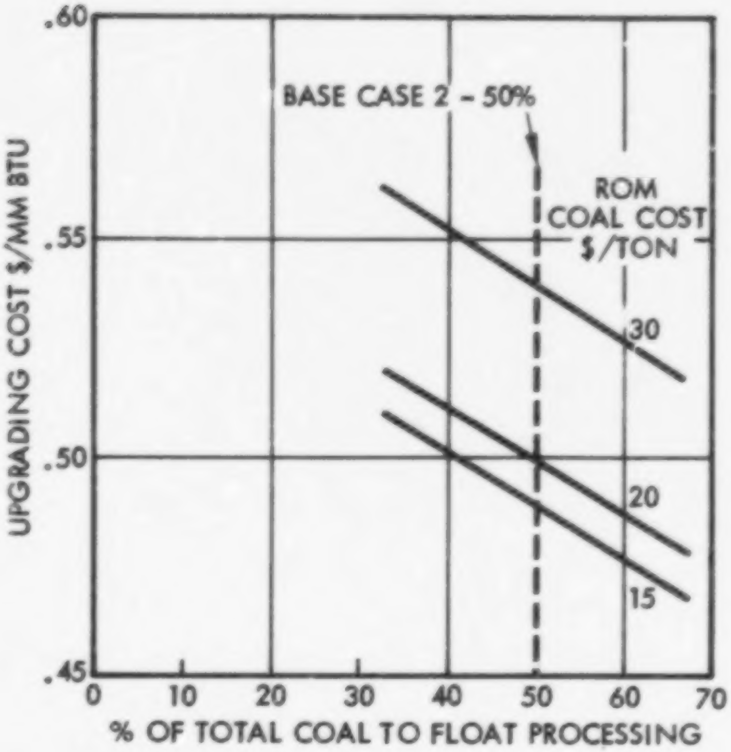

Figure 46. Base Case 2. Upgrading Cost vs. %
Total Coal to Float Processing

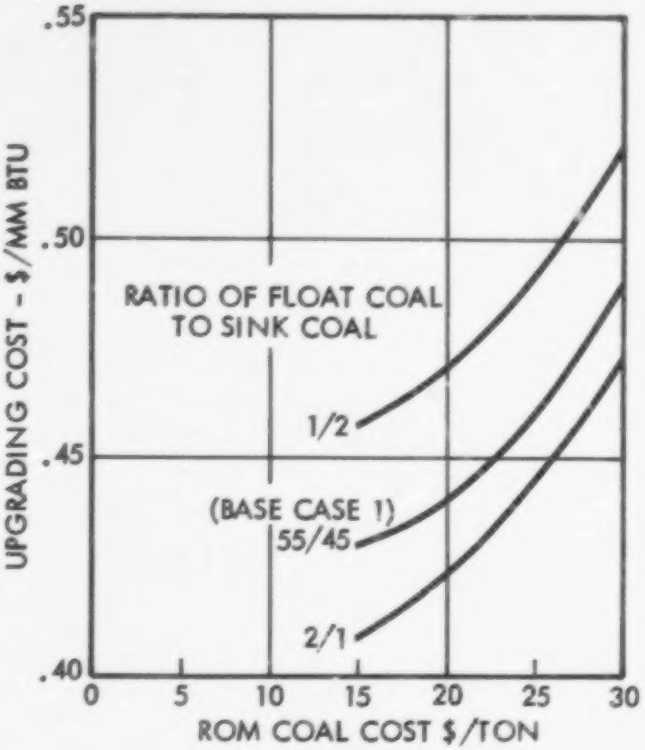

Figure 47. Base Case 1. Upgrading Cost vs. ROM Coal Cost

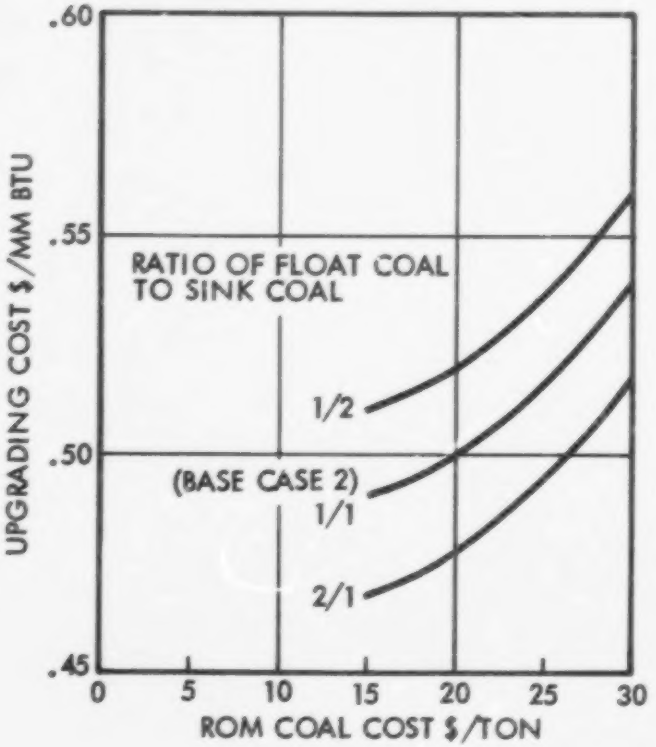

Figure 48. Base Case 2. Upgrading Cost vs. ROM Coal Cost

# 9. VENDOR TESTING

## 9.1 GENERAL APPROACH

The current RTU equipment is intended to emphasize study of the desulfurization reaction portion of the Meyers Process. Operations which may be evaluated are coal transfer and leach solution contacting, elevated temperature-pressure depyritization, and solution regeneration. A filtration operation is also included in the RTU to facilitate coal and solution separation and handling as are solution storage facilities. The specific equipment which would be required to evaluate operations relating to efficient coal-leach solution separation, elemental sulfur removal via solvent extraction, leach solution concentration and neutralization, and coal drying is not included in the RTU. These operations would be required to demonstrate an integrated plant facility utilizing the Meyers Process.

The vendor testing task was intended to provide the necessary information on those unit operations not in the RTU through utilization of equipment supplier testing services. It was reasoned that basic data and scale-up information could be obtained in a timely cost-effective manner by allowing equipment vendors to apply their unit operation experience in testing coal prepared in the RTU. Thus, depyritized coal from the RTU would be packaged and transferred to each vendor. The vendor, following an approved test plan, would treat and return the coal for detailed analysis by TRW. The success of the vendor study was thought to be closely associated with the initial vendor selection and the detailed coordination, planning, and review of activities both in preparation and testing of the coal.

A vendor survey was completed and a vendor coordination and test plan was generated. An initial vendor coal supply was also obtained. Actual tests have been provided by one vendor to date. A processed coal supply is currently stored at the RTU which can be used for further vendor testing. The details of the above mentioned activities are provided in the following sections.

### 9.1.1 Equipment Suppliers Survey and Selection

A critical part of the vendor testing task was the selection of suitable vendors to be utilized. The general approach taken was to initially select vendor candidates for filtration, centrifugation, solvent stripping, coal drying and solution neutralization unit operations based on previous contacts. Then, the most promising vendor's, (based on scale-up capability, cost, schedule, ability to duplicate actual process conditions, sample sizes required and versatility for different tests at the same facility) would be determined. Finally a single vendor would be selected to test each unit operation and a specific cost, test plan, schedule etc., would be generated. Table 46 provides a list of the potential vendors considered for this program and the findings obtained from telephone inquiries and written correspondence. In general, each vendor was supplied with essentially the same type of information consisting of:

- Description of feed (composition, physical and chemical properties.
- Description of product (desired composition, physical and chemical properties).
- Description of tests desired (a matrix was provided showing the desired variables and parameters to be measured).
- Description of possible acceptable approaches (types of unit operations, sequences of operations, possible coreactant/contacting solution compositions, etc.).

By the conclusion of Phase 3 of the current program, initial vendor selections were completed. The selected vendors and the associated services which were anticipated are as follows:

Envirotech Corporation

- Filtration of coal slurry in leach or water solution, 4 tests, 40 gallons of slurry required (bench scale).
- Acetone slurry make-up, contacting and filtration, 4 tests (bench scale).
- Solvent stripping of acetone filter cake, 8 tests (bench scale).
- Neutralization of coal slurry leach solution filtrate, 8 tests (bench scale).

## TABLE 46. VENDOR SELECTION PROGRAM

| | | | Test Requirement (Per Test) | | |
|---|---|---|---|---|---|
| Vendor | Address | Unit Operation | Time (Days) | Quantity (Gallon) | Comments |
| Envirotech Corp. Eimco BSP Division | Salt Lake City, Utah | Filtration and Solvent Stripping | 15 | 10 Slurry | Small pilot scale equipment for leach solution and acetone slurry filtration and stripping. |
| | | Neutralization | 2 | | Will use material provided for filtration study for neutralization tests. |
| Bird Machine Co. | So. Walpole, Mass. | Centrifuge and Solvent Stripping | 3 (est.) | 300 Slurry (est.) | Able to do testing including acetone slurry repulping at pilot scale on 18" solid bowl centrifuge. Would run bench scale tests prior to pilot tests to determine operating parameters. |
| Artisan Industries, Inc. | Waltham, Mass. | Solvent Distillation | 4 | - | Able to run tests on 4" glass column. Artisan will provide acetone and makeup feed at their facilities. |
| Wyssmont Co., Inc. | Ft. Lee, N.J. | Drying | 5 | 6000 | Test can be performed at the facilities in Ft. Lee on a small pilot scale dryer or on a large pilot dryer at another location. Either drier will provide design information for scale-up to full size. |
| | | Drying | 4 | 5 | |

(Continued)

TABLE 46. (Continued)

| Vendor | Address | Unit Operation | Test Requirement (Per Test) Time (Days) | Test Requirement (Per Test) Quantity (Gallon) | Comments |
|---|---|---|---|---|---|
| Ametek Process | Temecula, Ca. | Filtration | 2 | 5 | Can only perform bench scale tests with acetone since pilot equipment is not explosion proof. Able to do leach solution tests at pilot scale. |
| | | Centrifuge | 2 | 5 | |
| | | Drying | 2 | 5 | Test could be done using a small pilot dryer with solvent recovery capability. |
| Dorr-Oliver | Oakland, Ca. | Filtration | 5 | 300 | Cannot handle acetone slurry due to inadequate ventilation. Leach solution tests could be done at pilot scale. Testing could be done [illegible] bench scale for acetone slurry. |
| | | Centrifuge | | | |
| Joy Manufacturing Co. Denver Equipment Division | Denver, Col. | Filtration | - | - | Testing can only be done at bench scale since the pilot equipment is not corrosion resistant to leach solution. |
| | | Solvent Stripping | | | |

Bird Machine Company

- Centrifugation of leach solution or water coal slurry, 4 tests, 1200 gallons of slurry required (pilot scale).
- Centrifugation of acetone slurry, 4 tests, 4 gallons acetone slurry required (bench scale).

Wyssmont Corporation

- Drying of acetone wet cake, 6 tests, 30 gallons acetone wet cake required (bench scale).

Artisan Industries

- Acetone stripping, 6 tests (bench scale).

Test plans and implementation strategy needed to develop firm agreements for the studies were also developed and are discussed in the following paragraphs.

### 9.1.2 Vendor Test Implementation Plan

A detailed test plan was developed to define the test and data requirements for the RTU vendor testing effort(10). Briefly, the approach presented in the plan was to initially contact vendors with testing capabilities, select the most promising vendor, prepare specific test objectives, prepare and package RTU processed coal for testing, process the coal at the vendor test facility under several parametric sets of conditions, and to observe and evaluate the tests through on-site test monitoring and by analysis of feed and product materials.

At the conclusion of each test series, the vendor was to provide documentation of the following:

- Run date, duration.
- Type and size of coal used.
- Equipment model, operating conditions, and controls.
- Feed rate, mass closure, energy consumption where obtainable.
- Observations during the run, such as uniformity of product, thickness, apparent wetness, and problems.
- Conclusions and recommendations in terms of feed rates, effectiveness of the unit operation for purpose intended, and limiting factors for equipment usage.

It was also planned to obtain full-scale process equipment costs and utilities requirements based on the vendor test data for use in conceptual full-scale design work.

### 9.1.3 Vendor Testing Results

During RTU operation (Phase 3 of the current program), initial small-scale laboratory drying tests were conducted by Wyssmont. These studies were performed to obtain preliminary drying characteristics of acetone wet Martinka coal in tray dryer type equipment. It was anticipated that this preliminary data would minimize the chances of nonproductive testing at the more costly larger pilot scale. For purposes of this preliminary study, one gallon of 14 mesh x 0 coal product (Martinka, Coal #1), was obtained from the RTU on 30 June 1977. The RTU processing consisted of coal-water contacting and mixing at 212°F for approximately 6 hours followed by filtration. Since there was no added iron sulfate in solution and since oxygen was not utilized in the reactor, it was anticipated that the coal would experience negligable reaction. The RTU processed coal was further processed in TRW laboratory facilities to simulate downstream Meyers Process operations prior to the final drying (i.e., acetone extraction) step. The acetone wet cake was then sent to the Wyssmont laboratories for testing. The specific procedure followed in preparing the cake for shipment to Wyssmont was as outlined below.

1. Water wet cake from the RTU was dried in vacuum overnight.
2. To 5.43 lbs. of the dry coal, 0.81 lbs. of acetone was added, resulting in a 14.9% w/w acetone wet cake.
3. The cake was placed in a 1-gallon can in an inert $N_2$ atmosphere and was then shipped to Wyssmont.

The Wyssmont processed coal samples were returned to TRW for chemical analysis. Those samples were evacuated under hard vacuum for 24 hours at 212°F. During the 24 hours all condensables were captured in cold traps. The condensed volatiles represented 0.59 percent of the starting material by weight. The condensed volatiles were subjected to mass spectrometric analysis and were found to be 83% w/w acetone and 17% w/w water. These results indicate that the original 14.9% w/w acetone wet cake was reduced to 0.49% w/w acetone in the small-scale test apparatus.

In addition to the input/output analysis and results described above, samples of the cake were removed from the drying apparatus at Wyssmont as a function of drying time and examined for weight loss (presumed to be acetone-water volatilization). Samples were removed from the 250°F drying apparatus after 15, 30, 40, 50 and 60 minutes of total drying time. They were found to contain approximately 2.0% w/w, 1.8% w/w, 0.9% w/w, 1.1% w/w and 0.6% w/w moisture respectively. It should be noted that these results are somewhat crude in nature due to the lack of sophistication in equipment at the Wyssmont facility and the inherent nature of the test apparatus (dust evolution could not be detected if minor and therefore may interfere with results). However, the final 60-minute weight loss result agrees very well with the more precise mass spectrometric analytical results.

With regard to full scale applicability, Wyssmont personnel indicated that although the small scale vendor tests indicated residual acetone levels of 0.5% w/w, a residual level of 0.1% w/w acetone would be attainable through proper adjustment of dryer gas recirculating rate, and temperature, and solids residence time.

### 9.1.4 Coal Supply for Vendor Studies

In preparation for the vendor studies plan discussed in 9.1.2, coal was collected from the RTU filter belt during experiments 03-01, 03-02, and 03-03, after steady state operation had been attained. Table 47 describes the coal compositions and the coal quantities obtained for future vendor testing.

## 9.2 VENDOR TESTING CONCLUSIONS

An obvious need currently exists to demonstrate total Meyers Process operability beyond that of the limited RTU capability. The vendor testing approach still appears to be a very advantageous method of obtaining the desired processing information and scale-up data. Based on the enthusiastic response of the vendors contacted and the degree of flexibility found in several of the selected test facilities, it is anticipated that a great deal of meaningful information could be obtained in an efficient, cost effective manner. A system encompassing RTU sample generation, sample collection, sample documentation, sample analysis before and after testing, and TRW-vendor communication and technical support has been demonstrated. Samples of RTU processed coal are stored

TABLE 47. COAL CAKE COLLECTED FOR VENDOR TESTING
(14 MESH X 0 MARTINKA, RTU COAL #3)

| Container Designation | No. of Containers* | Cake Wt. lbs. | Average** Coal Cake Composition, % w/w (Except Heat Content), Dry Basis | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ash | Heat Content, Btu/lb | Total Sulfur $S_T$ | Pyrite Sulfur $S_P$ | Sulfate Sulfur $S_S$ | Organic Sulfur $S_O$ | Elemental Sulfur $S_E$ | Iron Fe | Cake Moisture |
| 0301-1/6 | 6 | 2700 | 13.0 | 13260 | .91 | .18 | .06 | .49 | .18 | .23 | 15.5 |
| 0302-1/6 | 6 | 2800 | 12.0 | 13390 | 1.03 | .17 | .07 | .60 | .19 | .26 | 19.8 |
| 0303-1/8 | 8 | 3900 | 12.5 | 13265 | 1.04 | .14 | .11 | .59 | .20 | .25 | 19.1 |

---

* 55 gallon steel open head drums with insertable polyethylene liners and header.

** Exp. 03-01, average of 12 samples and their analyses.
Exp. 03-02, average of 15 samples and their analyses.
Exp. 03-03, average of 13 samples and their analyses.

and awaiting possible future shipment to the selected vendors. In summary, the availability of vendors, vendor facilities, plans, and material is such that the vendor test program could be started at any time. It is therefore recommended that vendor testing of RTU generated coal product be reinstituted at the earliest possible time to obtain the desired process scale-up data.

# 10. MATERIALS OF CONSTRUCTION EVALUATION

Tests were performed on the TRW Coal Desulfurization Process RTU to evaluate the effects of the process reactant environment on selected materials of construction. Following initial shakedown tests in which acidified leach solution and/or coal-water solutions were used, the plant was put into operation using the full operational cycle. Experimental test sequences were conducted over the periods 12 October to 23 November 1977 (Experiment 01) and 5 January to 11 January 1978 (Experiment 03).

The corrosive medium was an abrasive slurry/leach solution of variable composition containing coal, water, 1 to 5 percent sulfuric acid, 0.1 to 5 percent ferric and ferrous sulfate, and blended oxygen. Oxygen partial pressure ranged from zero up to about 45 psig. Chemical analysis of the leach solution also showed the presence of traces of chloride ions (28 to 107 ppm) and fluoride ions (15 to 32 ppm). The reactor was operated at temperatures up to $275^{o}$F and total pressures up to about 80 psig.

The RTU is generally constructed of 316L Cres (stainless steel). Therefore the plant equipment itself serves as an extensive metallurgical specimen. Other materials of construction were evaluated through the use of metallurgical test speciments which were installed inside the R-1 pressure vessel (the primary reactor) just prior to Experiments 01 and 03. The test specimens included coupon test samples and stress-corrosion test samples made of a variety of metals, non-metals and non-metallic coatings and liner materials. Metallic and elastomeric erosion test orifice plates were place in the reactor pump-around loops.

Experiment 01 ran in product test environment for approximately 170 hours until leaks developed in the piping/valve system, forcing shutdown. The RTU was inspected and the metallurgical test specimens were removed for analysis in late

November 1977. During shutdown, the R-1 reactor was repaired. Deeply corroded areas were filled with 316L weld rod material and smoothed by grinding. Shallow pits were removed via grinding only. New test specimens were installed and the plant was restarted on 5 January 1978. Experiment 03 ran for approximately 80 hours before an unexpected pump failure forced shutdown. After draining and cleaning, the internals of the R-1 reactor and the metallurgical test specimens were again inspected. The results of the inspections and analyses of the R-1 reactor and associated piping, and of the metallurgical test specimens installed in the RTU are reported in Section 10.1 and 10.2 respectively.

## 10.1 INSPECTION AND ANALYSIS OF RTU EQUIPMENT

After each shutdown, an inspection and analysis of corroded or failed RTU components was carried out. Of particular interest were parts of the piping system, the R-1 reactor, and the R-2 mix tank.

The first inspection, in November 1977, showed the effects of approximately 250 hours of operation at elevated temperatures. The first 80 hours were shakedown runs. Some of these runs were without coal or oxygen. In all but one, a very low concentration (less than 0.2%) of iron existed in the system. Sulfuric acid concentrations during shakedown ranged from zero to 4 percent. During Experiment 01, the plant ran for about 170 hours at normal operating temperature (230$^{o}$F to 275$^{o}$F) under conditions of high iron and acid concentrations. The specific operating conditions are delineated in Section 6 of this report.

The second inspection, in January 1978, showed the effects of about 80 hours of operation during Experiment 03 at 230$^{o}$F. A slurry containing only a small amount of iron (less than 0.2%) was used. The types of corrosion noted after Experiment 03 were different than those found after Experiment 01, suggesting that different methods of attack were present.

### 10.1.1 Piping System

After Experiment 01, various components from the discharge lines and return loops for Cells 3, 4, and 5 of R-1 were inspected where leaks were observed. These lines were exposed to leach solution at 230$^{o}$F to 270$^{o}$F. The flush port fittings in the discharge lines all contained leaks, some obviously associated with welds. The Cell 4 return line had a leak at the reducer weld while the Cell 5 line had a leak in a formed bend area.

Figure 49 shows the Cell 5 flush port fitting. Salts were visible at leaks in the fitting. Large pits were present on the inside surface. In addition, many smaller pits formed. Cross sectioning the sample at one of the smaller pits revealed a porous "spongy" structure, Figure 50. The porous structure penetrated about 25% of the way through the wall. Little evidence of weld sensitization was found while some degree of incipient attack was noted on machined inside surfaces.

The Cell 5 return line was sectioned and a large pitted area was found (Figure 51) which was associated with the pipe weld. No sensitization was noted and the metallurgy of the parent metal and weld appeared normal. The attack in the weld area appeared to follow grain boundaries. While the inside surface appeared to be shallowly pitted when viewed normal to the surface, cross sectioning revealed that the porous material extended the full thickness of the pipe and caused perforation.

Pitting was observed in reducers where a crevice condition existed, Figure 52. These pits were not associated with welds. Portions of pipe which fit into the reducers were badly attacked due to crevice corrosion also. Flanges throughout the system showed evidence of crevice corrosion beneath their gaskets as shown in Figure 53. In contrast, inspection after Experiment 03 showed no crevice corrosion on the flanges.

Inspection of the failed P-1 feed pump after Experiment 03 indicated that the chrome plated 316L rotor had been severely attacked by the slurry. The plating had flaked away, exposing the 316L, which then eroded and/or corroded away until pump tolerances grew and pumping capability was lost.

Electron microprobe analysis (EMP) was performed on several failed 316L components. The flange in Figure 53 was probed to determine the chemistry of an area pitted by crevice corrosion. Both the pitted area and a deposited crystal were analyzed. The EMP indicated high Si and O and significant P, Fe, and Cr in the corroded areas.* Analysis of a pit from a pipe end,

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* High = >10%
Significant = 1-10%
Trace = <1%

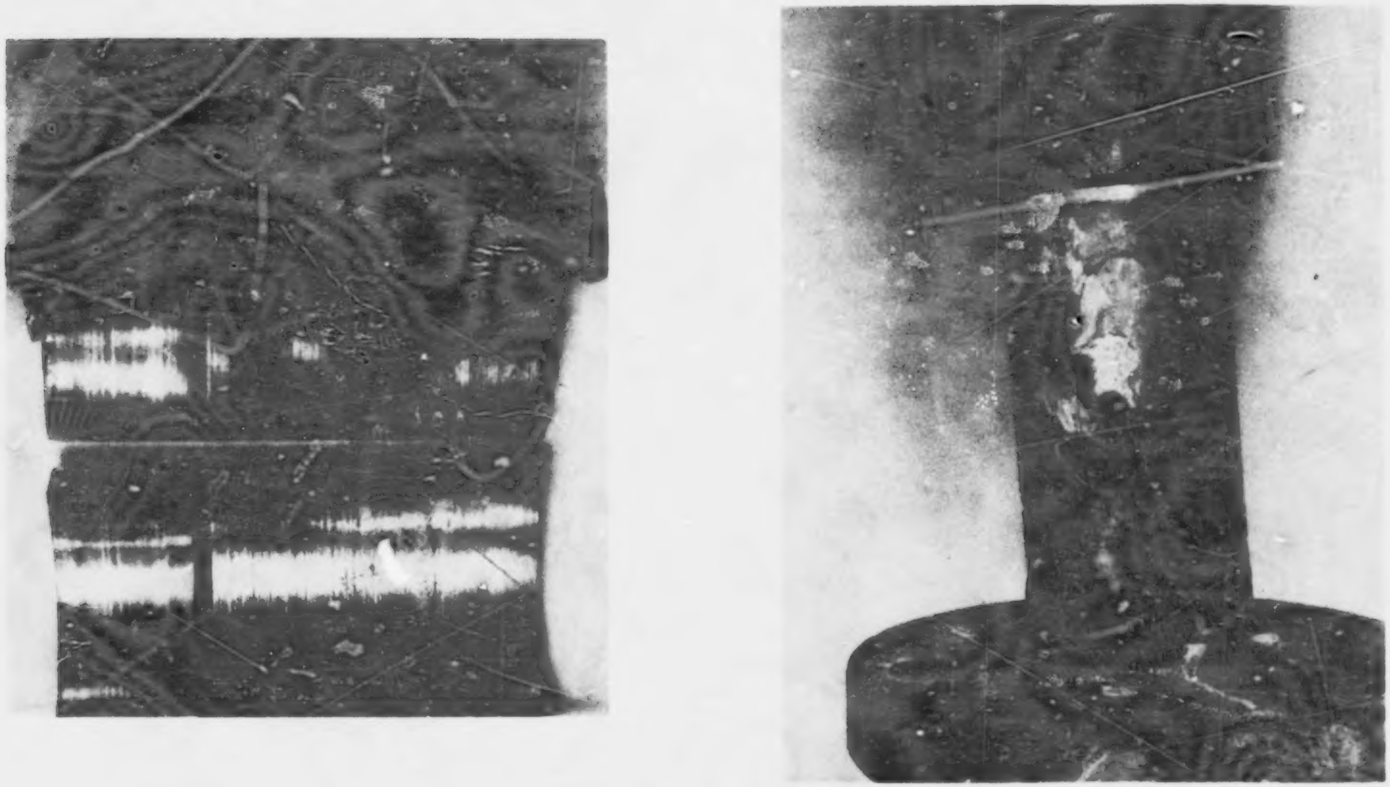

Figure 49. Flush Port Fitting

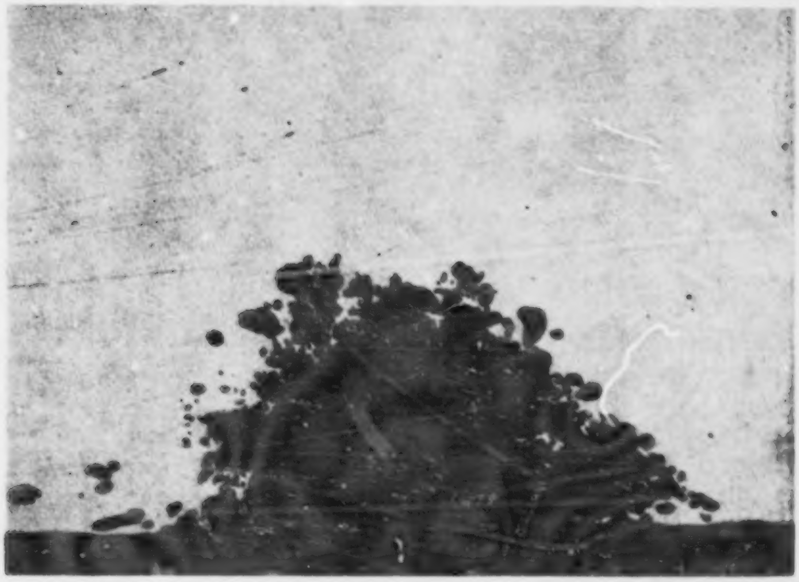

Figure 50. Porous Spongy Structure

indicative of pitting corrosion, showed a different chemistry. High Ca, K, Fe, S, and O and significant amounts of Cl, Mn, Cr, Si, and Na were found. A common feature of all the pits analyzed was that Mo and Ni, if present, were only found in trace amounts, even though they comprised 2 and 12 percent respectively of the starting metal (316L).

R-1 Reactor

The R-1 reactor is constructed of 316L stainless steel and is approximately 3 feet in diameter and 15 feet long. It is divided into five cells Connections between the vessel's many nozzles and ports and the plant's piping/valve system are welded and/or bolted at gasketed flanges.

Visual inspection of the reactor after Experiment 01 showed crevice corrosion at the manways and at weir/ring interfaces, and pitting corrosion near the "salt line" (water line) in the reactor. The area below the water line was green indicating a ferrous sulfate deposit while that above the water line was orange-red indicating ferric sulfate. A cell by cell summary of the observations is given below.

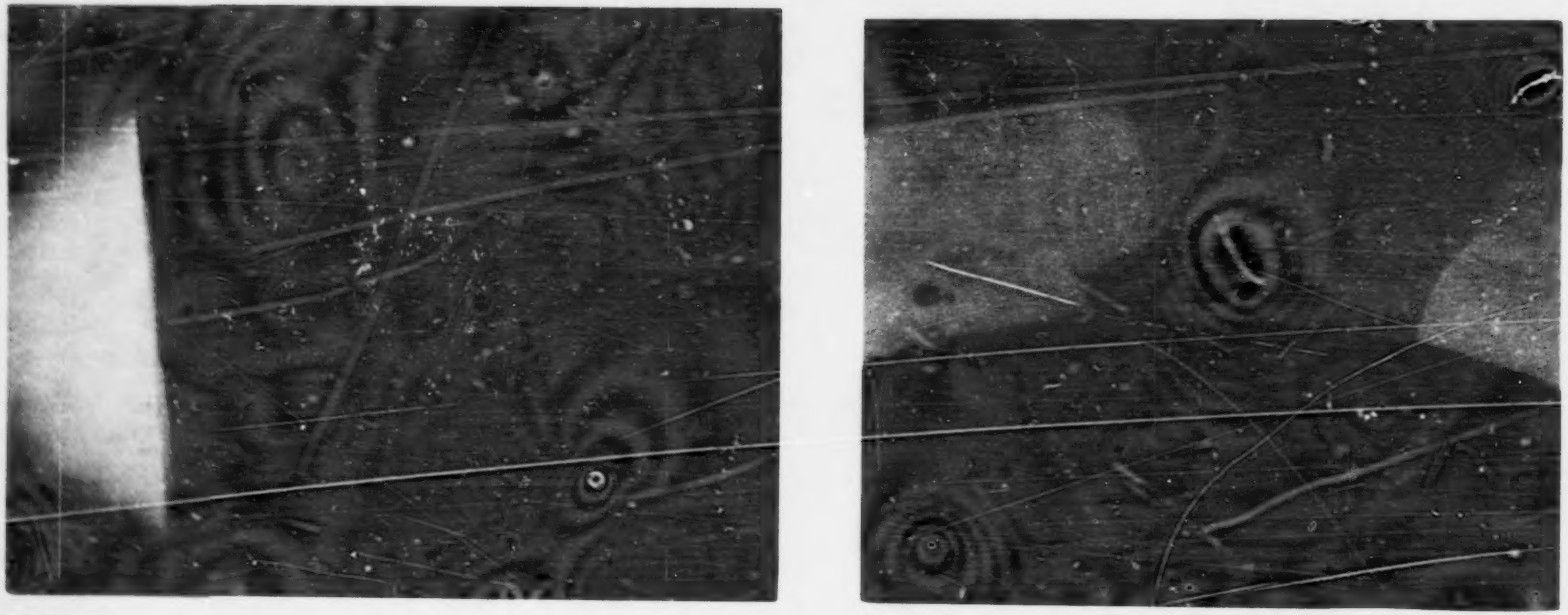

Figure 51. Pipe Weld Corrosion

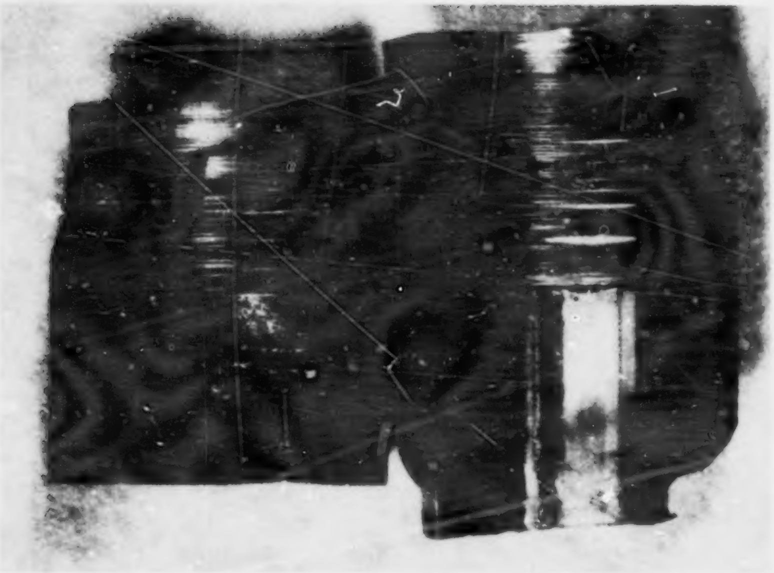

Figure 52. Crevice Corrosion in Reducer Fitting

Cell 1. There was no evidence of pitting or crevice attack. Wall deposits especially on the manway side, made inspection difficult. Some small pits were detected at the mixer port flange.

Cell 2. No evidence of pitting.

Cell 3. Several large pits were noted at or near the water line. A .38-inch x .12-inch x .015-inch deep* pit was found at the weld near the #2 bulkhead on the opposite side from the port. Other small pits were visible in this area. The metal around these pits crumbled when probed with a knife blade revealing a porous structure similar to that noted on the piping/valve components. There were about 30 of these small pits ranging from .015-inch to .030-inch diameter. After probing, the dimensions of the larger exposed areas were .188-inch x .125-inch x .060-inch deep, .125-inch diameter x .125-inch deep and .100-inch diameter x .040-inch deep. Other pits were noted near the center of Cell 3 at a small port. One of these pits was .250-inch x .188-inch x .030-inch deep. There were also six interconnected

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*Note: Depths were estimated.

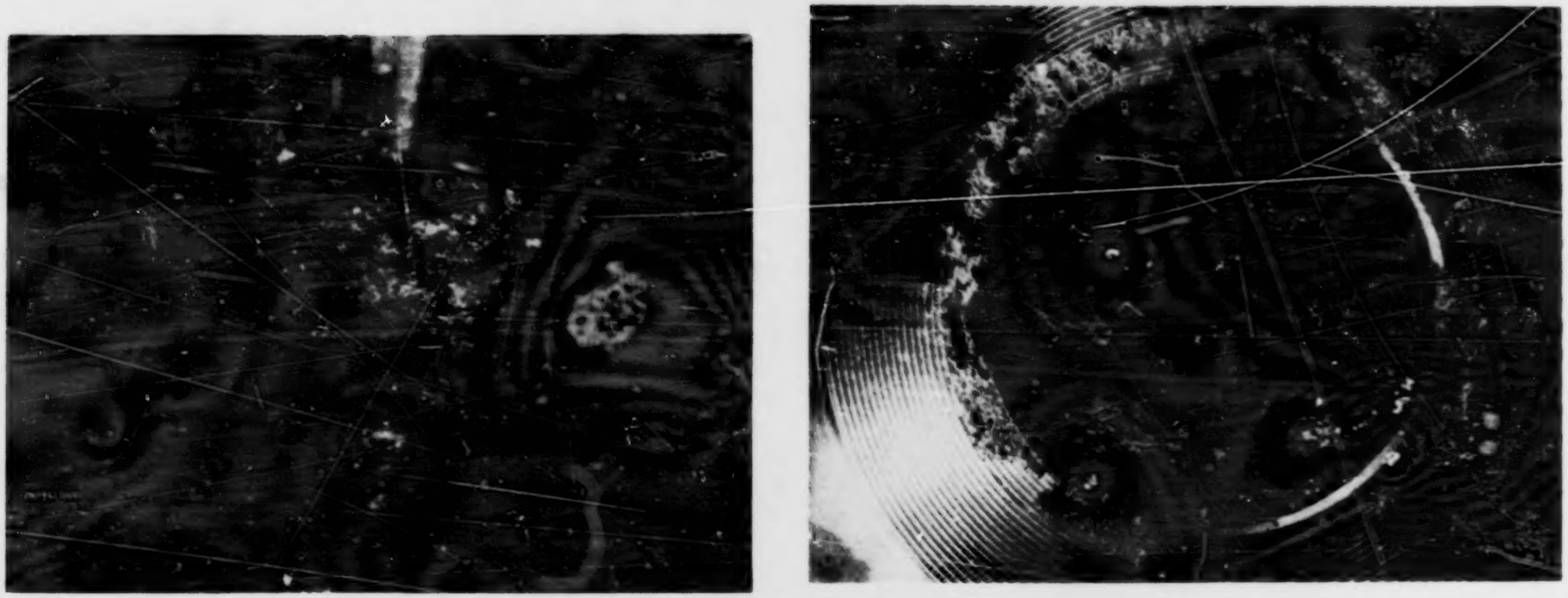

Figure 53. Flange Crevice Corrosion

pits in this area all approximately .030-inch deep. The largest of these was .125-inch diameter. These various pits were determined to be typical of those found in numerous other regions within Cell 3.

Cell 4. Heavy deposits were found in Cell 4 making inspection difficult. Two pits were found near the #3 bulkhead on the far side. Their sizes were .188-inch x .125-inch x .090-inch deep and .250 inch x .090 inch x .030-inch deep. On the port side, a .125-inch diameter x .030-inch deep pit was found near the #5 bulkhead. The bulkheads (weir rings) between Cells 3 and 4 and between Cells 4 and 5 were attacked on the edges. Large areas could be scraped away with the knife blade revealing a porous, crumbling, structure. The weir nuts were attacked, especially where they were welded to the bulkheads. The baffle nuts and bolts were severely attacked and could be separated by hand, see Figure 54. The weir baffle was attacked at the edge, Figure 55.

Cell 5. Porosity and pitted structure which could be scraped away was found near the #4 bulkhead on the far side from the manway. Exposed areas were .188-inch x .125-inch x .060-inch deep, .125-inch diameter x .030-inch deep, .250-inch x .125-inch x .030-inch deep and .250-inch diameter x .030-inch deep. The bolts holding the baffles crumbled away as did the nuts. The lower part of the bracket was pitted and the bracket-to-wall weld had a .125-inch diameter x .030-inch deep pit. Two pits were found on the port side near the dome weld. These were .250-inch diameter x .030-inch deep and .125-inch diameter x .020-inch deep.

The TE 56 temperature probe, although appearing solid and shiny, crumbled when scraped with the knife blade exposing a large area of porous, heavily attacked material (Figure 56). The corrosion apparently originated at the tip-to-probe weld. EMP analysis showed the probe base metal to be 316L. High amounts of Si and O were found in the corroded area. Iron, Cr, and Ni were either undetected or present in only trace amounts.

Inspection of the R-1 reactor internals after Experiment 03 showed only minor signs of the spongy pitting that was observed after Experiment 01. This type of attack was visually evident only at the water line and on a welded attachment. However, many smooth bottom pits were observed. General pitting occurred where grinders had been operated in repairing the reactor (Figure 57).

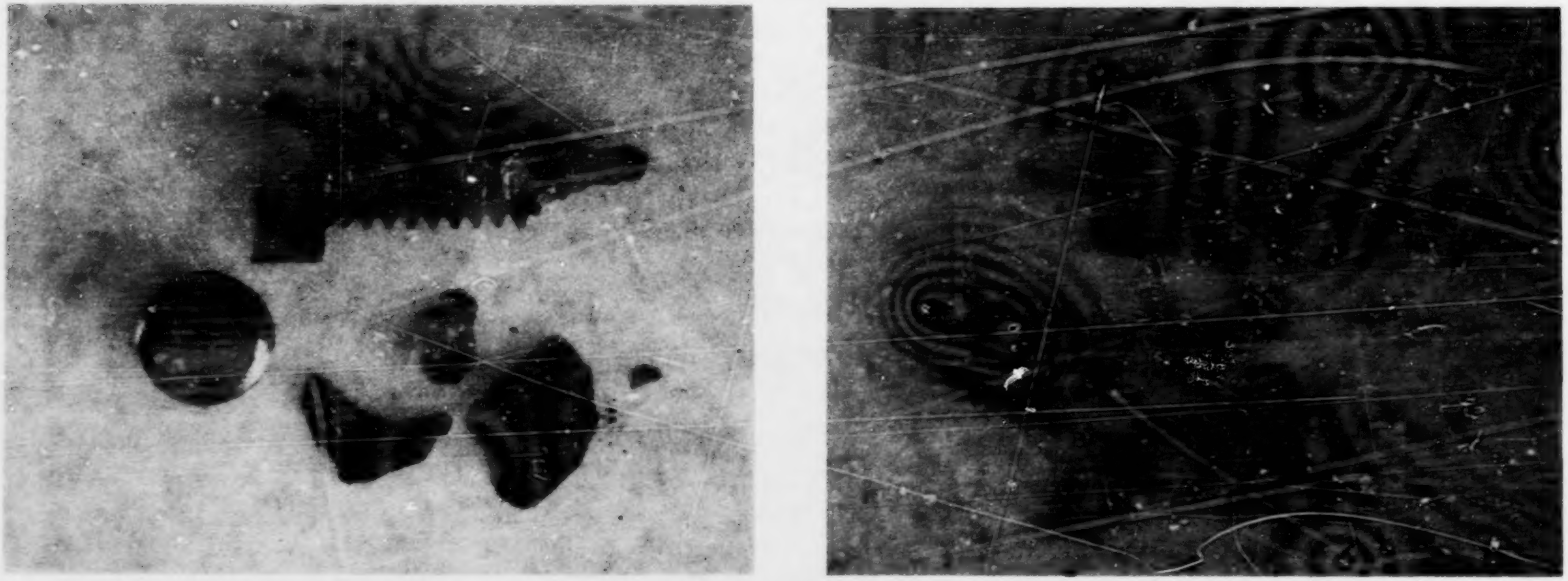

Figure 54. Baffle Bolts and Nuts from R-1 Cell 4.

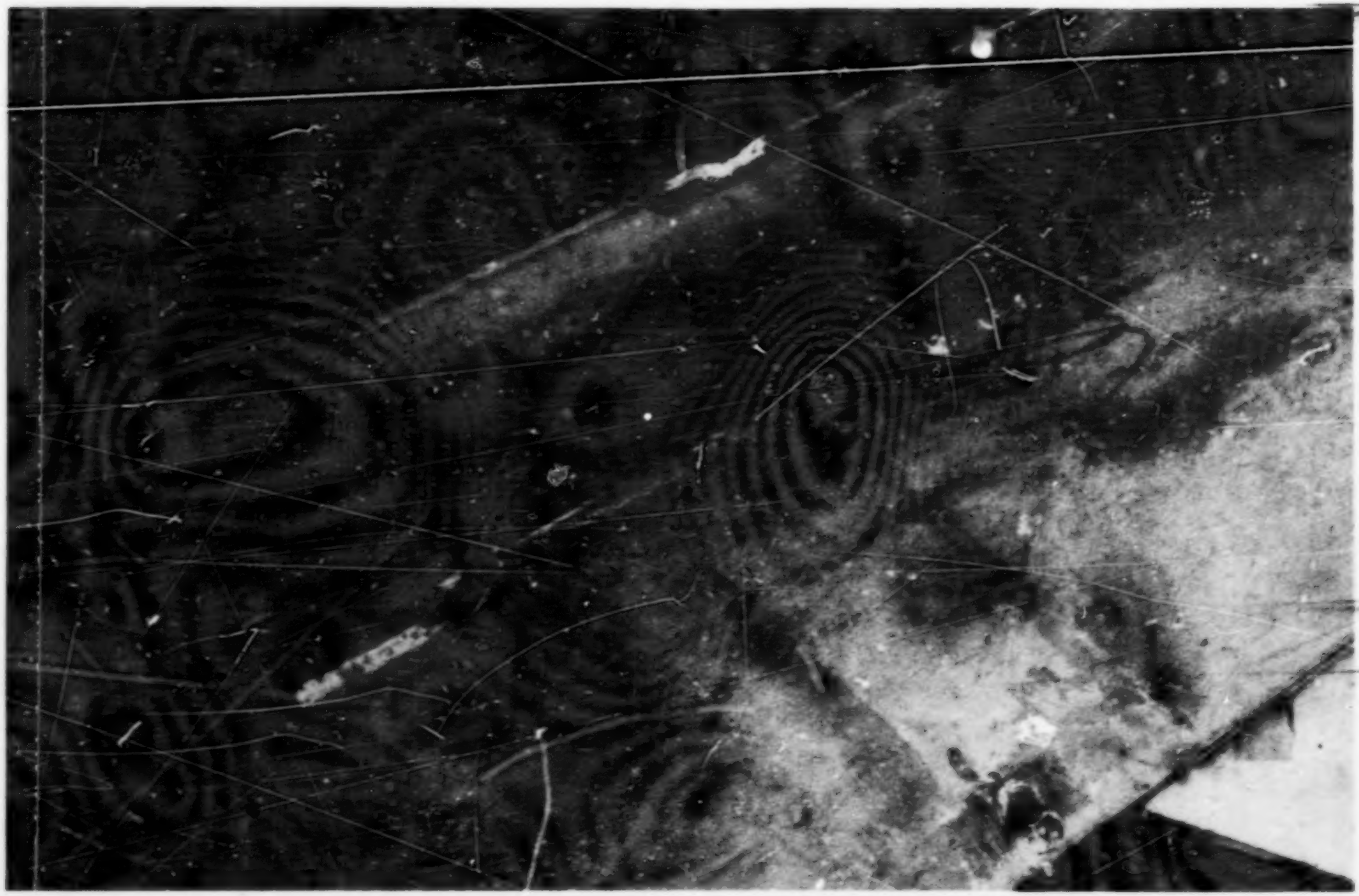

Figure 55. Weir Baffle

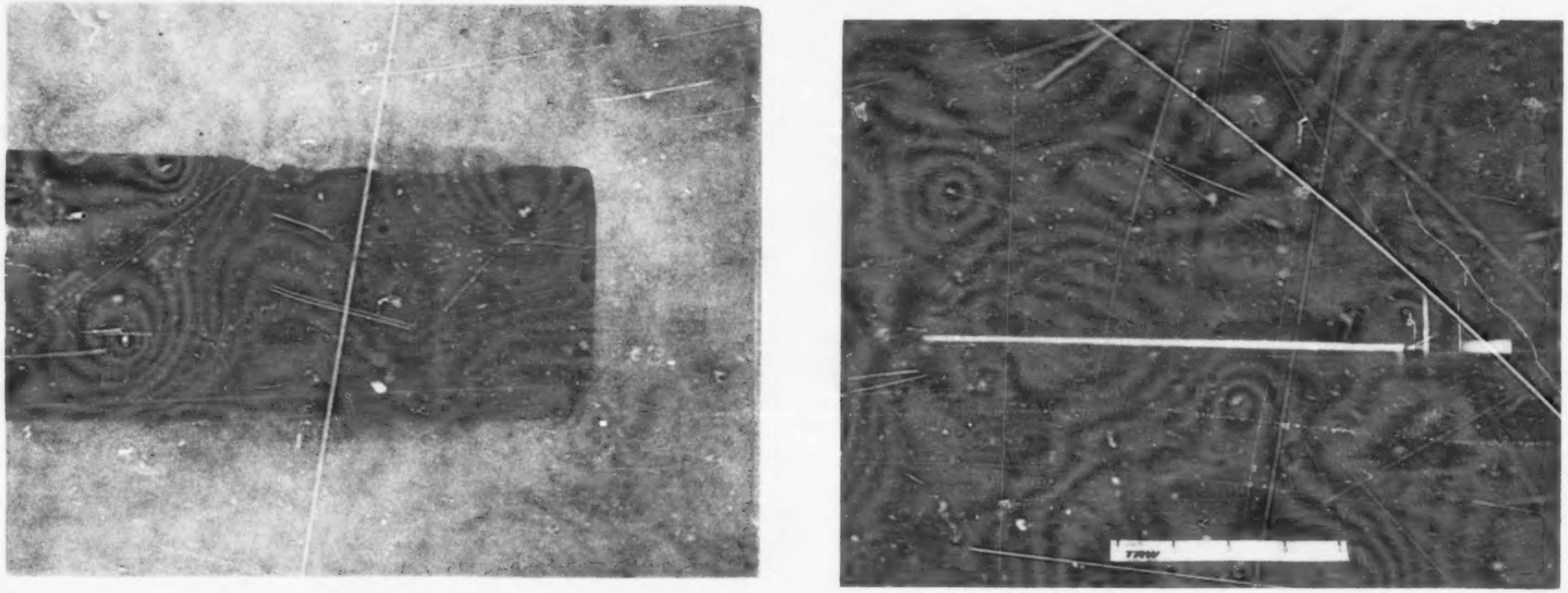

Figure 56. TE-56 Thermocouple Probe

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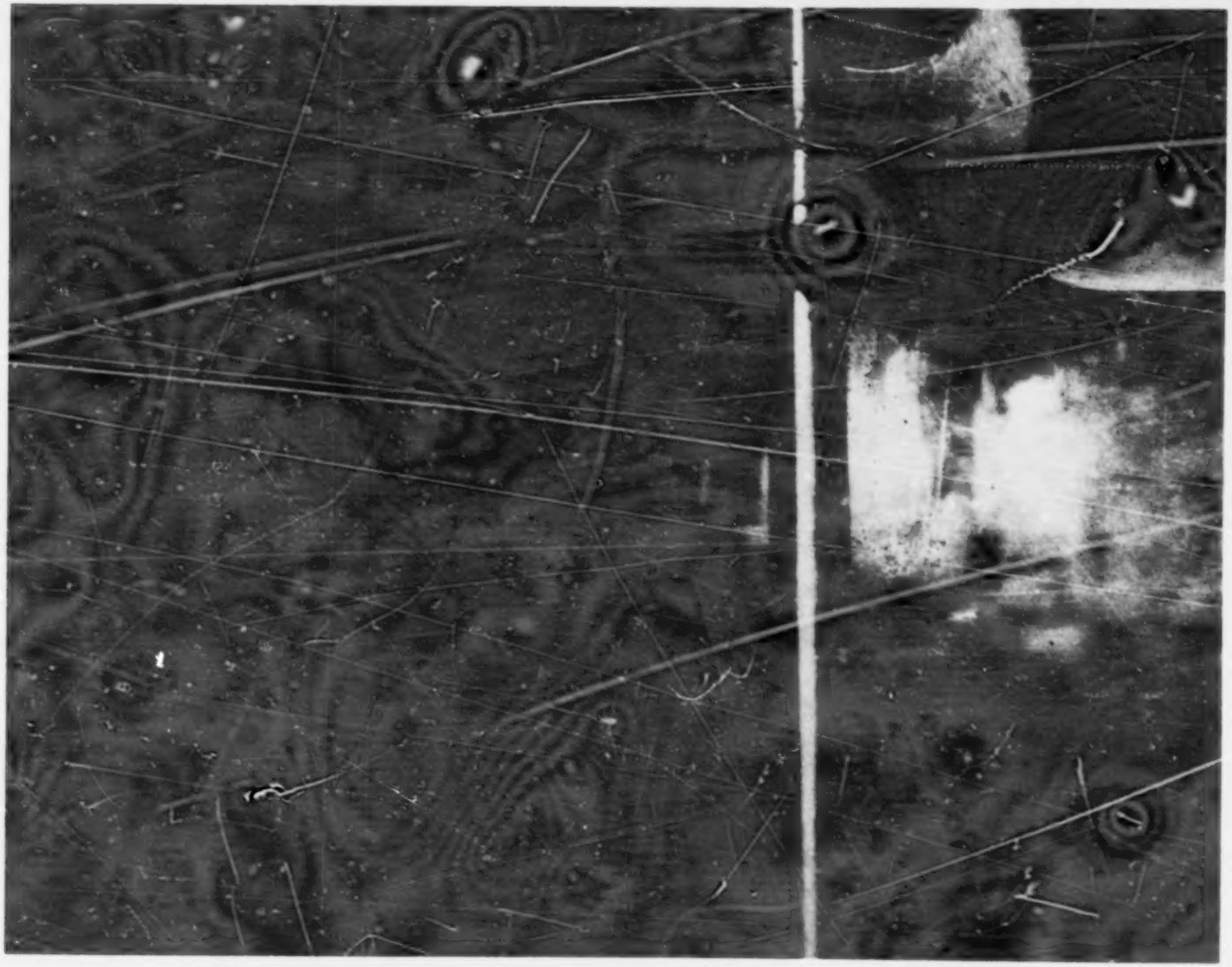

Figure 57. R-1 Reactor Internals AFter Experiment 03 Showing Pits Where Grinders Had Operated

Pitting was evident at welds and on free surfaces (Figure 58). No crevice corrosion was visible.

### 10.1.3 T-2 Mix Tank

The T-2 mix tank was inspected on 9 December 1977. Some crevice corrosion was noted on the manway flange and door in the seal area. The mixer port flanges were unattacked. In general, the internal surfaces of the mix tank were not attacked by pitting or crevice corrosion. No crevice corrosion was noted on the baffles, bolts or nuts. The temperature probes were also not attacked. The only attack noted was under a piece of masking tape which had been left adhered to the wall in Cell Number 3. A shallow pit had formed in the crevice caused by the tape. The pit was .250-inch x .188-inch x .015-inch deep. Two or three pits (about .100-inch diameter) were found on a blade from one of the mixers. Incipient pitting was noted on the bore of the propeller. The weir actuator shaft was attacked in the area of attachment to the weir plate (crevice condition) and the corresponding weir plate guide showed a possible pit. It should be noted that while the T-2 mix tank experienced the identical coal/slurry stream that the R-1 reactor saw, the temperatures in T-2 never exceeded 212$^{O}$F since it is an atmospheric pressure vessel. Also, there is no oxygen injection into T-2. These differences are believed to relate to the much lesser degree of corrosion experienced in T-2 as compared with the reactor R-1.

## 10.2 ANALYSIS OF TEST SAMPLES

The primary types of attack which RTU materials of construction must resist are erosion-corrosion in high flowrate areas, stress corrosion cracking (SCC) in high stress areas, pitting corrosion, crevice corrosion, and general corrosion. The tests described in this section were designed to predict the performance of a variety of materials used in the corrosive environment of the R-1 reactor.

Materials samples in the form of metal and alloy corrosion coupons, stress-corrosion coupons, coated and lined coupons, and non-metallic coupons were mounted in the R-1 reactor in Cell 3. A 316L and Teflon rack was constructed and the specimens were mounted using Ti-6Al-4V bolts, 316 Cres bolts, and 304 Cres nuts. The bolts and nuts were sealed (overcoated) using a Hypalon elastomer coating. In addition, metallic and elastomeric orifice

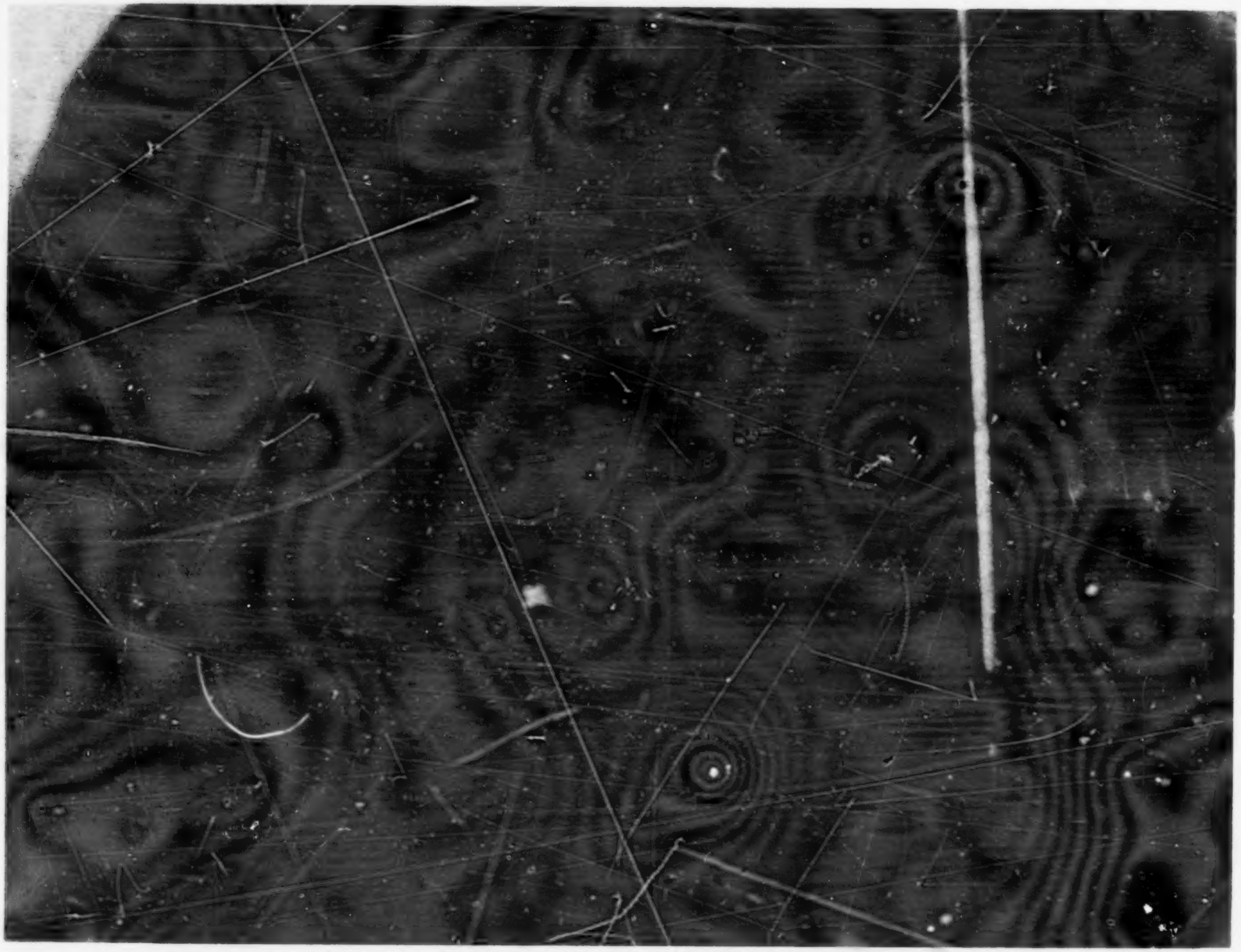

Figure 58. R-1 Reactor Internals After Experiment 03, Showing Smooth Bottom Pits at Welds and on Free Surfaces

plates were installed in the cell discharge and return lines to assess erosion characteristics of these materials. All coupon and orifice plates had areas where crevice conditions existed. A summary of the results of the inspection and analysis after removal on 29 November 1977 are given in Table 48. The observations noted for samples removed during both the November 1977 and January 1978 inspections are presented below.

### 10.2.1 Corrosion Coupons and SCC Specimens

Figure 59 shows corrosion coupons and SCC samples attached to the mounting rack prior to installation in the R-1 reactor. After removal, the samples were cleaned, weighed, and inspected for signs of corrosive attack.

Metal Corrosion Coupons. Inspections of samples tested in Experiment 01 suggest there are at least two distinct corrosion mechanisms operating, namely corrosion in crevices and pit formation on free surfaces. Once corrosion has initiated, a spongy porous structure forms which can tunnel under the surface to honeycomb the substructure. The crevice attack appear to be caused by a concentration cell(20), with oxygen the most probable species experiencing the concentration gradient. The pitting corrosion appears to be triggered by $C\ell^-$ ion and sustained by the presence of $Fe^{3+}$ ion and possibly complicated by localized deposits causing crevice conditions.

A third type of pitting was observed during Experiment 03. Pits which formed did not have a spongy, porous structure but were smooth with rounded bottoms. Test conditions for Experiment 03 were less severe than Experiment 01 (lower temperature, lower iron and halide ion concentration, shorter duration). However, it is unclear what mechanism of attack caused the round bottomed pits.

The effects of the corrosive environment on specific coupon materials is summarized below.

- 316L Cres Stainless Steel. A 316 Cres sample was put in as a control. Crevice pitting occured under the bolt head and the nut during Experiment 01 resulting in a weight loss of 0.14 percent. Inspection of the coupons after Experiment 03 revealed smooth bottomed pits but no crevice corrosion (see Figure 60).

- 304 Stainless Steel. The samples exhibited smooth bottom pits, but no crevice corrosion when inspected after Experiment 03 (see Figure 61).

## TABLE 48. COUPON CORROSION TEST RESULTS - 29 NOVEMBER INSPECTION

| Material | Result |
|---|---|
| **Metals:** | |
| 316 Cres | Crevice Corrosion |
| Pure Nickel | Completely Dissolved |
| Inconel 601 | Crevice Corrosion<br>Noncrevice Pitting |
| Inconel 617 | Crevice Corrosion<br>Noncrevice Pitting |
| Inconel 625 | Crevice Corrosion |
| Incoloy 825 | Crevice Corrosion<br>Slight Non Crevice Pitting |
| Titanium | No Attack |
| Lead | No Attack<br>No Pitting<br>Yellow - Red Coating |
| Non-Metallics: | |
| FRP | Edge Cracking<br>Severe Weight Loss<br>Resin Bond Attack |
| Ashland 197/3 + AT-8-4 | Blistered<br>Embrittled<br>Cracked |
| Ashland 800/801L-68-26 Furfuryl Alcohol Resin | Surface Etched<br>Crazed<br>Pitted |
| Ashland 800-10-19 | Severe Weight Loss<br>Surface Etching |
| Ashland 7240-4-37 Unfilled Polyester Resin | Blistered<br>Discolored |
| Ashland 7241-6-27 Unfilled Polyester Resin | Blistered<br>Edge Cracking<br>Discolored |
| Ashland 72L + 5b-1-23 | Severe Weight Loss<br>Etched |
| FRP Pultrusion | Embrittled<br>Cracked |
| Plasites 4020, 4030, 4092 Vinyl Ester Coatings on Steel | Some Etching<br>Discoloration |
| Ceilcote 252 | Etched<br>Cracked |
| Coatings: | |
| Kynar 202/205 | Delaminated<br>Peeled<br>Coating Undamaged |
| EA919 Epoxy | Badly Attacked |
| Viton A | Unaffected |
| AF-E-332(EPDM) | Unaffected |

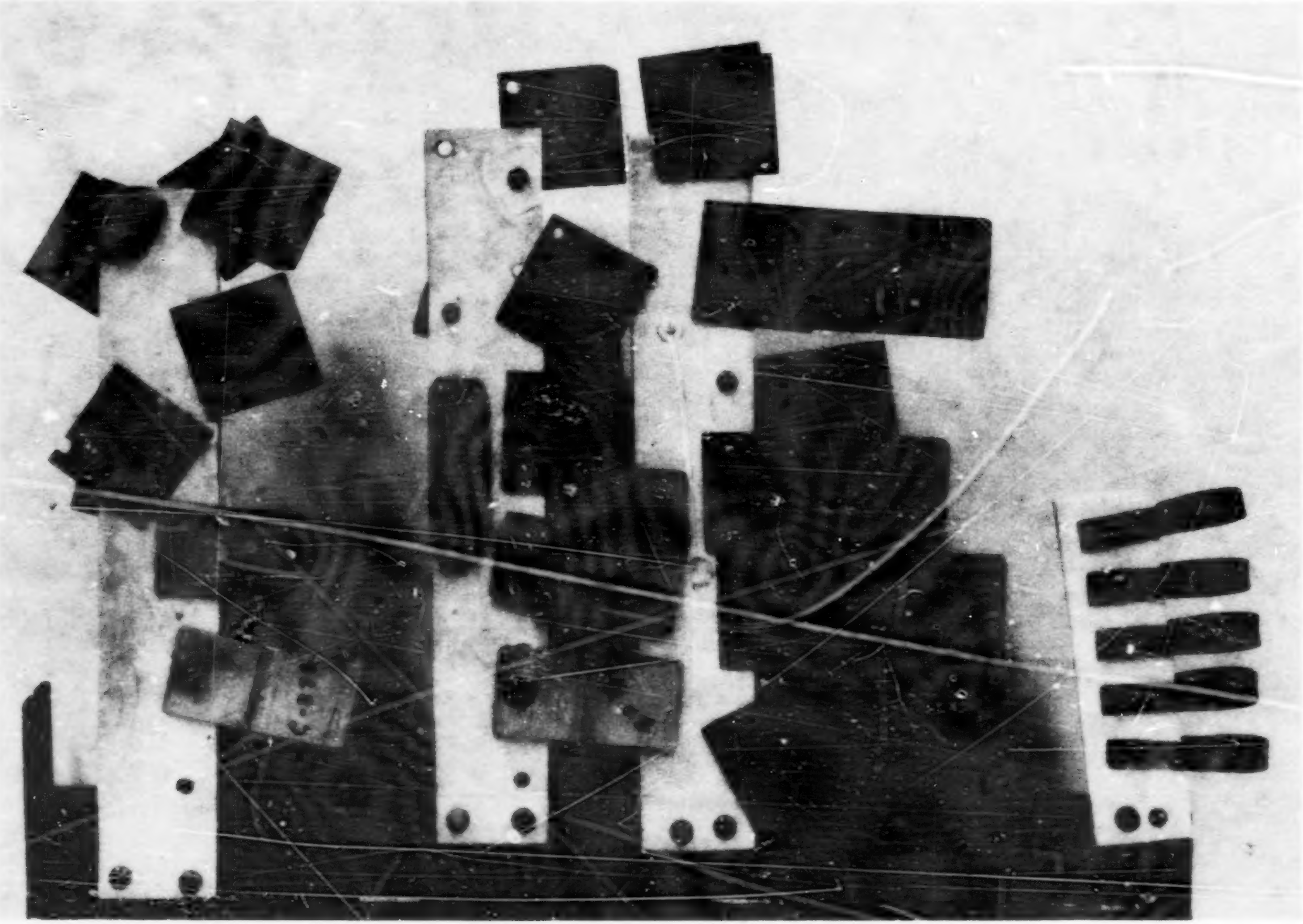

Figure 59. Coupon Mounting Rack and Test Specimens

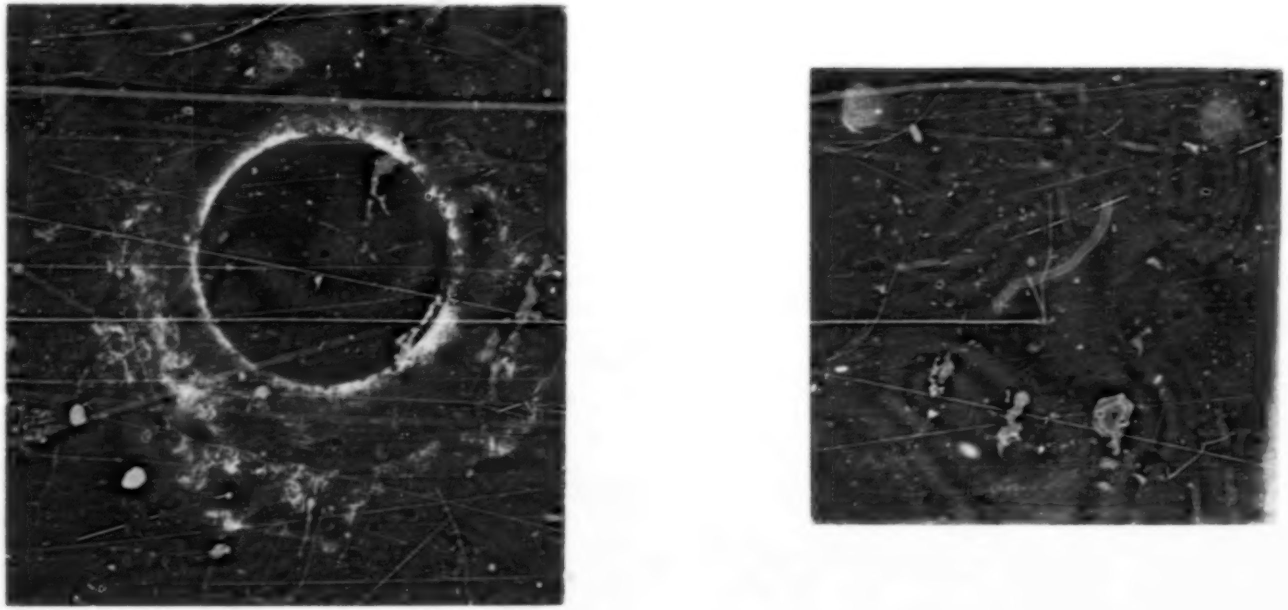

Figure 60. 316L Cres Coupons Showing Signs of Crevice Attack During Experiment 01 (L) and Smooth Bottom Pitting During Experiment 03 (R)

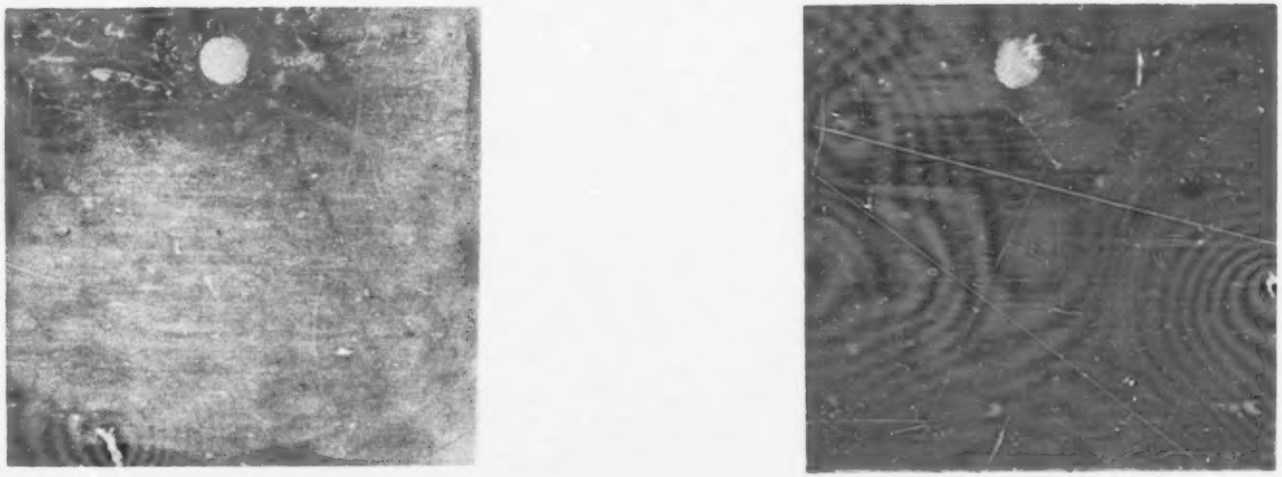

Figure 61. 304 Stainless Steel Coupons from Experiment 03 at and Above Water Line (L) and Below Water Line (R)

- Nickel Base Metals and Alloys. Coupons of pure nickel and of various Inconel and Incoloy alloys were tested. The pure nickel coupon dissolved completely during Experiment 01. Inconel 601 showed a weight loss in excess of 4%. It pitted badly around the bolts which attached it to the mounting rack, and also showed significant attack in noncrevice areas. The Inconel 617 coupon was subject to similar crevice corrosion and noncrevice pitting, but experienced only a 0.18% weight loss. Inconel 625 and Incoloy 825 samples were not as prone to noncrevice attack, but did show significant crevice corrosion (Figure 62). Weight losses of 0.055% and 0.31%, respectively, were recovered. Coupons of Hastelloy G and Hastelloy C-276 mounted in the R-1 reactor during Experiment 03 showed no visible signs of corrosion when removed and examined (Figure 63).

- Titanium. Samples of commercially pure titanium (Ti-65A) and of Ti-12 alloy were tested in Experiment 01. Neither coupon was visibly attacked (Figure 64). Weight losses were less than 0.01% for both coupons. Ti-50A coupons tested in Experiment 03 are also shown in Figure 64). They showed no visible signs of corrosion. Normally, titanium can be attacked by low concentrations of sulfuric acid. However, ferric ion suppresses this attack and acts as an effective corrosion inhibitor(21). The corrosive effects of fluorides are not known, however, the presence of calcium is known to tie up fluorides and thus act as a corrosion inhibitor in titanium applications(22). It is expected that enough calcium is present in the desulfurization environment to prevent fluoride attack.

- Lead. The lead samples had a yellow and red coating which was adherent. This was probably lead sulfate. The surfaces of the lead samples were not pitted (Figure 65).

Non-Metal Coupons. The nonmetallic coupons were removed from the R-1 reactor on 29 November 1977. The specimens were examined and evaluated for evidence of degradation and the results are as follows:

- Ashland 197/3-400-7, FRP High Temperature Polyester Resin. The fiberglass specimen underwent a 1.17% weight loss. The coated edges of the sample were cracked as was the surface gel coat. The fiberglass-to-resin bond was obviously attacked as evidenced by the pronounced fiber prominence at the specimen surface. The portion of the sample covered by the Teflon mounting plate was not discolored whereas the exposed portion was red-brown in color.

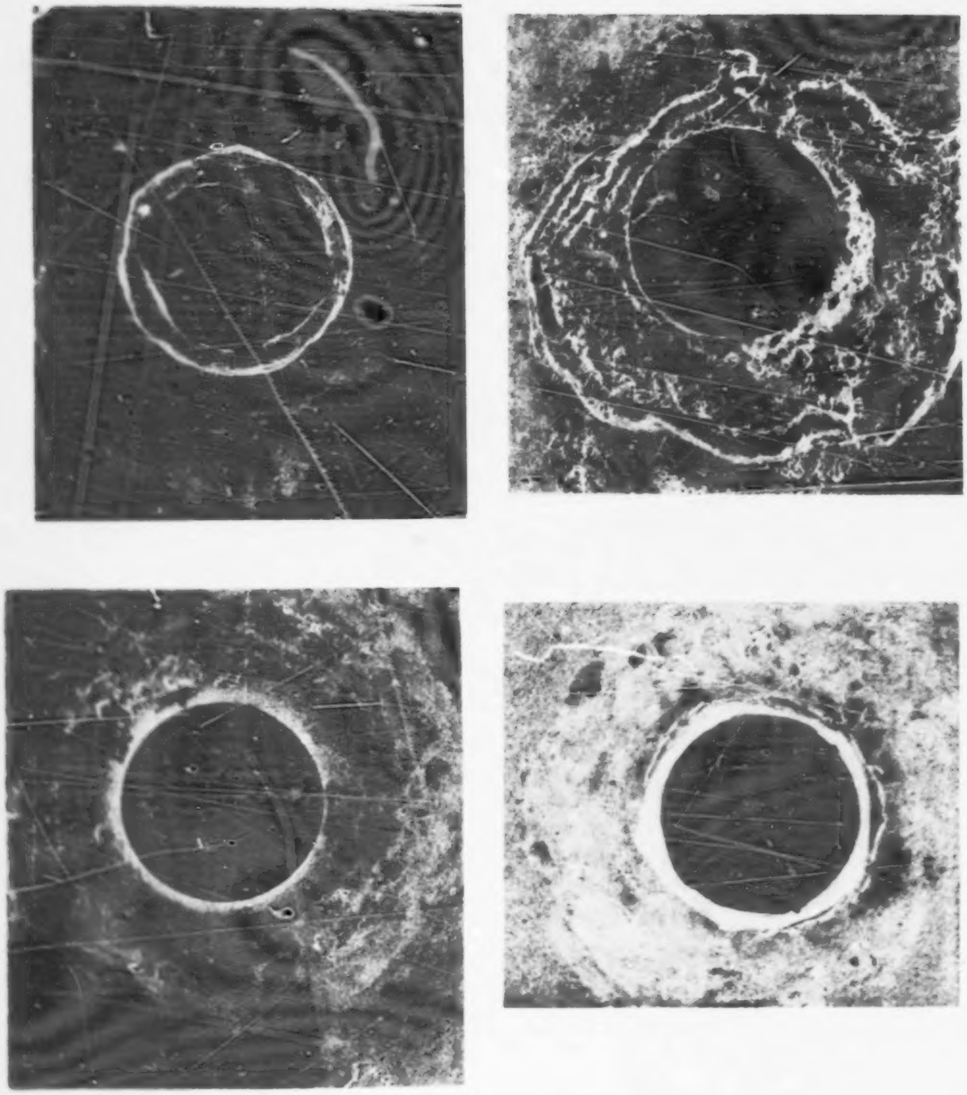

Figure 62. Inconel and Incoloy Alloy Coupons, 7.5X: Inconel 601 (Upper L), Inconel 617 (Upper R), Inconel 625 (Lower L), Incoloy 825 (Lower R)

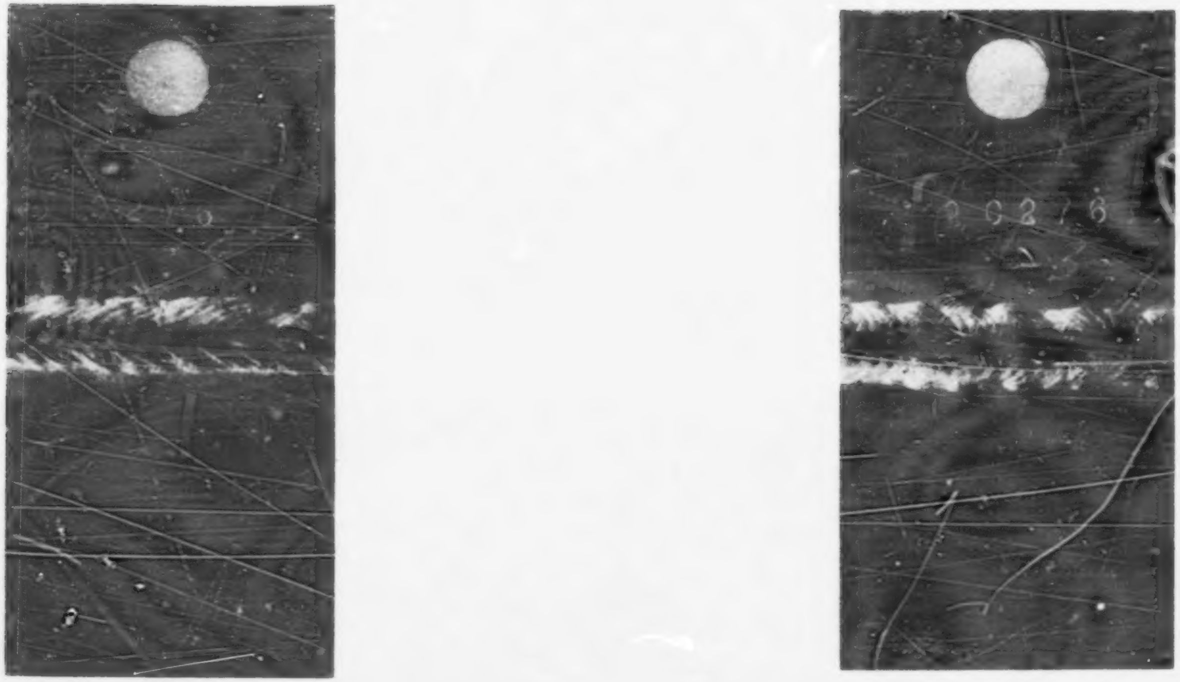

Figure 63. Hastelloy C-276 Coupons from Experiment 03 at and Above Water Line (L) and Below Water Line (R)

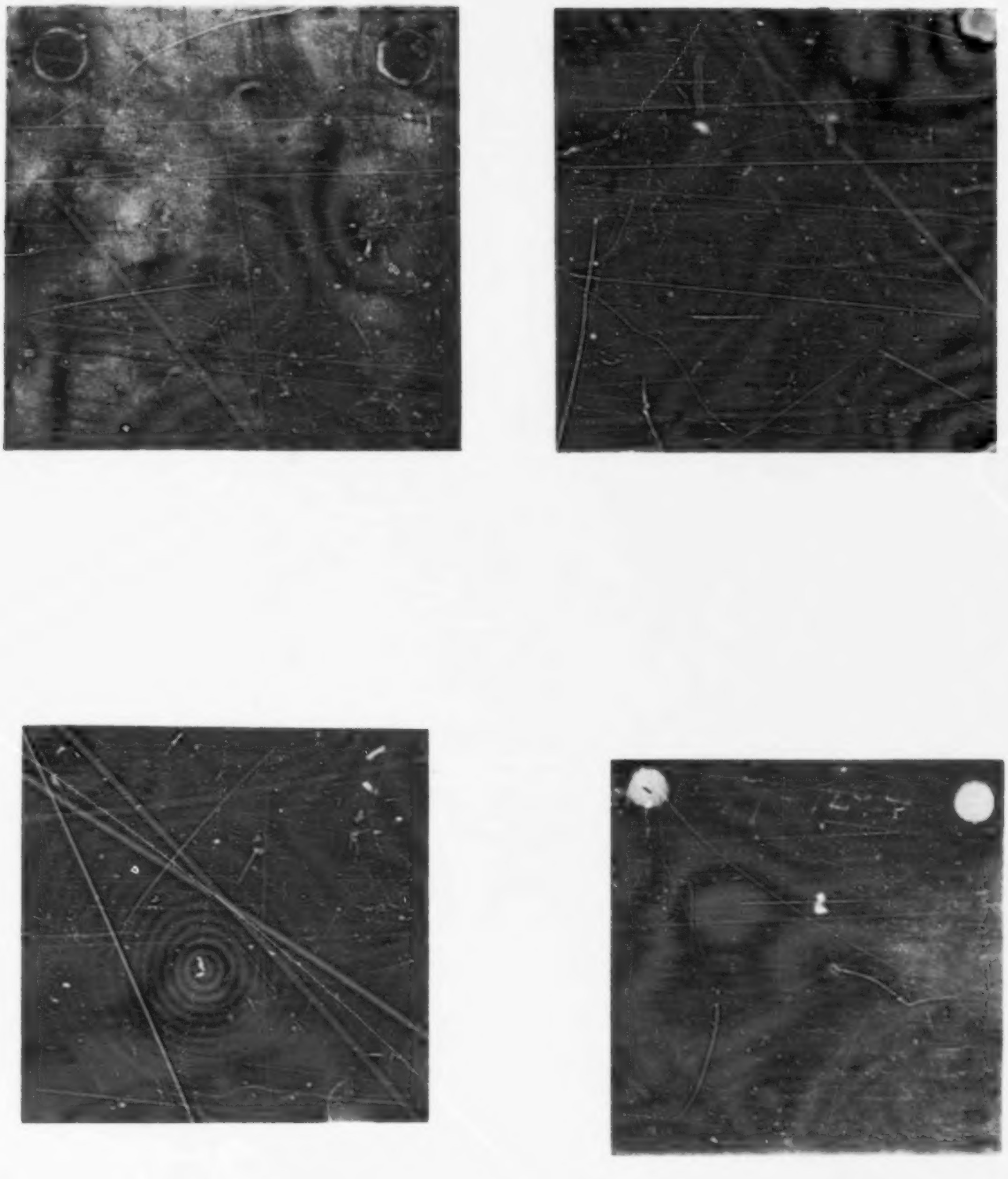

Figure 64. Titanium Coupons: Ti-50A (L) and Ti-12 (R), from Experiment 01 (Top) and Experiment 03 (Bottom)

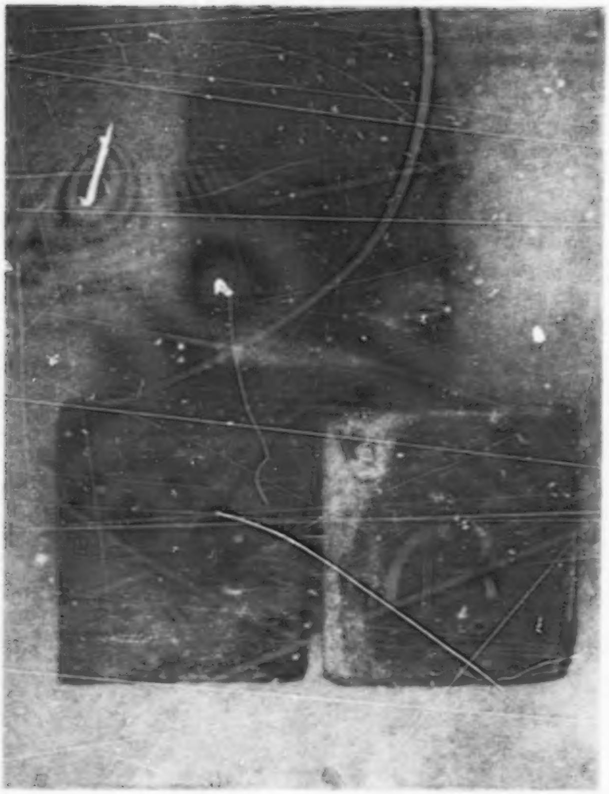

Figure 65. Lead Coupons from Experiment 01.
Surface Marked by Cleaning Operation.
No Pitting or Crevice Corrosion. 1.5X.

- Ashland 197/3 + AT-8-4 (Flame Retarded Version of 197/3). The surface of the specimen was blistered, but otherwise showed no visible signs of surface attack. The weight loss was almost negligible (0.50%). The sample, however, was drastically embrittled and the surface gel coat cracked during handling.

- Ashland 800/801L-68-26, Furfuryl Alcohol (Furan) Resin. The weight loss on this sample was low, 0.95%. The surface however, was badly etched except where covered by the Teflon mounting plate. Close examination of the surface showed it to be badly crazed and pitted. Surface veil fibers were exposed in the etched areas.

- Ashland 800FR-10-19 (Flame Retarded Version of 800/801). The weight loss on this sample was much more severe (2.50%). The surface etching and veil fiber exposure was similar to that of the 800/801 specimen. Again, the area under the mounting plate was largely untouched.

- Ashland 7240-4-37, Unfilled Polyester Resin. The weight gain on this sample was almost negligible (0.01%). However the sample was badly degraded. The surface was blistered and the glass reinforcement was very prominent due to degradation of the glass fiber-to-resin bond. The surface, except for the portion under the mounting plate, was a dark brown in color.

- Ashland 7241-6-27, Unfilled Polyester Resin. This sample showed degradation similar to that of the 7240 resin sample. The edge coating was cracked and in many places nonexistent. Additionally, the sample was warped.

- Ashland 72L + Sb-1-23, (Flame Retarded Version of 7240 and 7241 Resin). This specimen showed a 2.50% weight loss. The surface was badly cracked and etched except under the mounting plate. Additionally, small blisters were evident over all the sample surface and the edge resin coating was cracked.

- Fiberglass Reinforced Polyester Pultrusion. The specimen was badly embrittled and cracked during handling. The area around the mounting hole ripped during removal from the mounting plate.

Reinforced Coatings

- Plasites 4020, 4030, and 4092 Filled Vinyl Ester Coatings on Steel. These specimens, although showing some surface etching and discoloration, seem to survive. However, their long term resistance is impossible to predict on the basis of this short exposure.

- Ceilcote 252, Flakeglass Filled Polyester on Carbon Steel. The surface of the coating appeared to be etched and the flakeglass filler exposed. The coating was cracked in one corner and the steel substrate exposed. This was probably the result of exposure to high temperature.

Coatings

- Kynar 202/205 Coating on Carbon Steel (Approximately .006-inch thick). The coating delaminated and cracked, probably because of differential thermal expansion and loss of adhesion due to moisture permeation. The steel almost completely corroded away, but the coating film looked like new.

- Kynar 202/205 Coating on 304 Stainless Steel (Approximately .006-inch thick). The coating was also cracked and peeled from this specimen although some was still adhering well to the surface. Some crevice corrosion was exhibited under the attachment hole after the coating was peeled back, however the 304 was largely protected by the Kynar.

- Kynar Sheet Stock Heat Sealed Coating on Carbon Steel (Pennwalt Sample). This specimen was thicker than the other Kynar samples. It showed no signs of degradation or substrate corrosion. The greater thickness of the sample enabled it to withstand thermally induced stresses.

- EA 919 Epoxy Coating On 304 Stainless Steel. This specimen was badly attacked. The coating could not be found and the stainless steel substrate crumbled into powder. The epoxy coating probably failed by hydrolytic breakdown of the resin in the hot oxidizing acid solution as well as thermal cracking and moisture permeation, which caused loss of adhesion to the steel substrate.

- Viton A Sheet Stock Bonded with RTV 732 Silicon Adhesive (Dow-Corning) to Carbon Steel. The Viton A was unaffected with no change in hardness and the steel substrate suffered minor corrosion because of a small leak in the RTV peripheral bond seal. The silicone showed signs of edge attack — small cracks and chalking. Viton A may be considered as a liner material; however, a suitable bonding and sealing agent must be found.

- AF-E-332 Sheet Stock (EPDM), Bonded to Carbon Steel with RTV 731 (Dow-Corning). The silicone rubber bond failed in adhesion to the EPDM (Ethylene Propylene Diene Monomer) surface and the carbon steel substrate completely dissolved. The EPDM showed no signs of degradation and change in hardness. The silicone seal suffered edge attack similar to the RTV 732; that is, extensive edge cracking and chalking. Although the EPDM itself was unaffected by process conditions, bonding and sealing of the material to the metal substrate presents a very difficult problem.

Stress Corrosion Cracking Specimens. None of the five SCC specimens (titanium, welded titanium, Incoloy 825, 316L Cres, Inconel 625) showed attack. However, the 304 Cres nuts failed, thus relieving the stress at some point during the run so that the test results are inconclusive. Some crevice attack occurred on the 316L Cres and the Incoloy 825 samples in the attachment area.

Coupon Mounting Rack. The 316L Cres support rack exhibited crevice corrosion at the mounting holes and localized pitting attack on its edges. This attack was not associated with welds. The Teflon portion of the rack was unattacked although cold flow had occurred under bolt heads which had been torqued to a high value. The PTFE Teflon mounting plates showed no signs of degradation, either from chemical attack or abrasion.

The Ti-6Al-4V rack mounting bolts appeared not to be attacked during the test but the 304 Cres nuts and 316 Cres bolts were severely attacked and, in some cases, dissolved.

The Hystl 6793-175 (glass reinforced, alumina trihydrate filler polybutadiene resin) mounting plate was softened and discolored. The plate cracked during handling and a cross section showed almost complete penetration of the leach solution into the material. Again, the hot oxidizing acid conditions appear to be the cause of the failure.

### 10.2.2 Orifice Plate Specimens

Five metallic and two elastomeric orifice plate specimens were tested during Experiment 01. The metallic plates were mounted using gaskets while the elastomeric plates acted as gaskets. The metallic materials tested were Inconels 601, 617, and 625, Incoloy 825, and Titanium 50A. The Inconels exhibited crevice corrosion under the gasket, although only a few pits were noted in the Inconel 625 plate. The corrosion was found on both sides of the Inconel 601 plate and on the downstream side of the Inconel 617 and 625 plates. Pitting on the exposed surface was noted for Inconel 601 and incipient pitting (mottled surfaces) for Inconel 617. Incoloy 825 was severely attacked in the crevice area on both sides of the orifice plate. The Titanium 50A plate was unaffected by the exposure and no corrosive attack was detected.

The Hypalon (chlorosulfonated polyethylene) orifice plate showed no signs of abrasion or tearing. The elastomer showed no decrease in cut resistance and in Shore A hardness. The Neoprene (chloroisoprene) orifice plate showed no signs of abrasion. However the Shore A hardness jumped ten points and material subjected to the hot sulfuric acid solution in the orifice area was torn due to a dramatic decrease in its localized tear resistance.

## 10.3 DISCUSSION

The observed corrosion in the coal desulfurization reactor and pump circuit components was extremely severe. The short operating time under full process conditions indicates that very rapid 316L corrosion rates are being experienced. The spongy, porous nature of some corroded areas suggests that serious damage can result even though visual inspection of the surface indicates little or no attack. In many cases, scraping what appeared to be a slightly attacked region resulted in material crumbling away to reveal large, deep pits. In one instance, a pit was detected in the R-1 reactor which penetrated about 25% through the wall.

The porous nature of the observed pitting is of critical concern. It appears that once a pit has been initiated, either by crevice conditions or by chloride attack on a free surface, that the corrosion follows metallurgical paths offering the least resistance, such as grain boundaries, stringers, cold worked areas, etc. This could result in multiple very small but relatively deep subpits within the main pit. At the root of these subpits, the local conditions would be much like a crevice so that an oxygen concentration cell can exist. This is, in essence, an electrolytic cell where the driving force to cause corrosion is an oxygen concentration gradient between the root of the subpit (low concentration) and the bulk of the solution (high concentration). These conditions would cause the subpit to rapidly extend producing the sponge-like structure. This possible mechanism could be worsened by high oxygen contents in the main slurry. It is interesting to note that neither crevice corrosion nor spongy structure was prevalent in the T-2 mixer which is oxygen free. While some crevice initiated pits were found in T-2, such as under the masking tape, the pits appeared to be shallow and smooth bottomed.

The coal desulfurization environment is extremely agressive to stainless steel, especially for the type of attack observed. The relatively high temperatures, low pH (pH of 1 to 2), crevice conditions, and high oxygen content of the slurry greatly accelerate crevice (concentration cell) attack. Pitting attack is greatly accelerated by the presence of halide ions and the reaction sustained by the presence of a metal ion, such as ferric or cupric ion, which can be reduced to provide the cathode reaction. Pitting rates are also greatly accelerated by high temperature, low pH, high velocity, and high oxygen content. Rough surfaces or surface deposits, internal or external stresses on metal parts, and metallurgical defects, such as inclusions, pores, and stringers, are especially susceptable to pitting attack. All of these factors play a part in the corrosion behavior of the desulfurization unit to varying degrees in different parts of the system.

During the course of the RTU corrosion study, it was discovered that similar material problems had been encountered in a Sherrit-Cominco copper ore processing pilot plant in Fort Saskatchewan, Alberta(18). In this process, aggressive slurries must be handled, which are similar to those encountered in the Meyers Coal Desulfurization Process. Significant corrosion problems were experienced before final material selections were made. Results from the Sherrit-Cominco pilot plant indicate that near ambient temperature storage tanks and thickeners constructed of fiberglass reinforced plastic have performed well. Where temperatures do not exceed 190°F, rubber lined mild steel has been used satisfactorily. At temperatures up to 230°F and 1% to 5% sulfuric acid concentrations, 316 Cres can be used if a high (50 to 100 g/ℓ) concentration of $CuSO_4$ is maintained. (Areas which do not contain significant copper sulfate concentration experience rapid failure of 316 Cres components.) Where temperatures reach 350°F to 400°F, titanium lines, valves, and heat exchangers are used and perform well. Pumps and lines subjected to severe abrasion and aggressive slurry compositions are constructed of Hastelloy C-276, selected as a result of a development program during which several other materials were eliminated. The above mentioned information appears to be very consistent with RTU related observations.

## 10.4 CORROSION STUDY CONCLUSIONS

The obvious conclusion drawn from the inspection and analysis of the system components and test samples is that unprotected 316L Cres is an unacceptable material for the R-1 reactor and pump around loops when they are operated at nominal process conditions ($O_2$ present, .2% to 5% iron, .2% to 4% sulfuric acid, and temperatures greater than $215^{o}F$).

Commercially pure titanium (Ti-50A) and titanium alloy Ti-12 appear to be suitable materials of construction for the R-1 reactor. The Ti-12 alloy may be required at flanges, mounting rings, etc., since it is more resistant to crevice attack than Ti-50A. The cost of pure titanium and Ti-12 is about 2 to 2-1/2 times the cost of 316 stainless but less expensive than Hastelloy C(23). This cost differential has been verified by a comparison of the existing RTU reactor cost and a 1978 vendor quote for a replacement reactor constructed of Ti-12. It should be noted that while titanium has performed well in short term test runs on the RTU, long term tests are needed to verify its acceptability.

Based on tests conducted during Experiment 03 and similar experience at Sherrit-Cominco, Hastelloy C-276 may also be able to withstand the hostile chemical environment of the Meyers Process reactor system. Hastelloy alloys are prime candidates for pump-around loop components.

Various metallic and non-metallic materials may be considered for component liners. Lead is a possibility as a lining material but long term corrosion rates and erosion resistance must be further evaluated. Most of the non-metallic samples were attacked to some degree by the high temperature sulfuric acid/iron sulfate solution. Notable exceptions were Viton A, EPDM, and Teflon. An effective means of bonding and sealing these materials to a metal substrate must be found before they can be considered practical as liners.

For applications in Meyers process equipment operating at or near leach solution normal boiling points (up to $213^{o}F$) in the absence of oxygen, results indicate that 316L and Fiberglass reinforced plastics (FRP) may be suitable materials of construction. There are also a number of coatings which also appear to be satisfactory in this application as discussed in Section 10.2.1. It should be stressed that all results are based on relatively short test durations. Therefore, an organized long term, materials testing activity would be desirable to conclusively determine the merits of the studied materials in Meyers Process applications.

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# 12. GLOSSARY OF ABBREVIATIONS AND SYMBOLS

## Abbreviations

| | |
|---|---|
| Abs | absolute |
| ASTM | American Society of Testing Materials |
| Btu | British Thermal Unit |
| cal | calories |
| eq | equation |
| Exp. | experiment |
| Kcal | kilocalories |
| No. | number |
| wt | weight |

## Symbols

| | |
|---|---|
| $A_L$ | Arrhenius constant in leach reaction $(\text{hours})^{-1}$ $(\text{wt \% pyrite in coal})^{-1}$ |
| $A_R$ | Arrhenius constant in regeneration reaction $(\text{minutes})^{-1}$ $(\text{atm})^{-1}$ (liters/mole) |
| C | concentration |
| $\Delta$ | difference in quantity following delta |
| $E_L$ | activation energy for pyritic sulfur leaching reaction, Kcal/mole |
| $E_R$ | activation energy for ferric ion regeneration reaction, Kcal/mole |
| $K_L$ | pyritic sulfur leaching rate constant (units same as $A_L$) |
| $K_R$ | ferric ion regeneration rate constant (units same as $A_R$) |
| $\mu$ | micron |
| P | total pressure, atmospheres |
| $P_{O_2}$ | oxygen partial pressure |
| R | gas constant, cal/mole - $^{o}$K |

Symbols (cont'd)

| | |
|---|---|
| $r_L$ | pyritic sulfur leaching rate, weight of pyrite removed per 100 wts of coal per hour |
| $r_R$ | ferric ion regeneration rate, moles per liter per minute |
| $S_n$ | elemental sulfur |
| $S_o$ | organic sulfur |
| $S_p$ | pyritic sulfur |
| $S_s$ | sulfate sulfur |
| $S_t$ | total sulfur |
| $T$ | absolute temperature, $^{o}K$ |
| $t$ | time, hours (leaching)-minutes (regeneration) |
| $W_p$ | pyrite concentration in coal, wt % |
| $Y$ | ferric ion to total iron ratio |

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16. ABSTRACT The report gives results of an evaluation of the initial performance of the Reactor Test Unit (RTU) for chemical removal of pyritic sulfur from an Appalachian coal. Operation of the plant--from its checkout and shakedown in September 1977 through January 1978--demonstrated that the RTU could be run continuously in three-shift operation to reduce the coal from 2.4 lb $SO_2$/million Btu to a level of 1.0 to 1.2 lb $SO_2$/million Btu, after rinsing and extraction of generated elemental sulfur. There was no measurable coal oxidation during processing and leach rates in the plant were greatly improved over bench-scale values. The leach solution/coal/oxygen environment was found to be corrosive to the installed stainless steel reactor, necessitating future upgrading to support additional testing. Bench-scale experiments showed that the leach solution can be used as a homogeneous dense-media to efficiently gravity-separate coal prior to processing. Beneficial engineering cost improvements are obtained based on using this approach, resulting in capital cost estimates of $68-69/kW and with $0.44-0.50/million Btu processing costs, including amortization of capital, for input coal costing $0.78-0.81/million Btu. Overall energy efficiency was 93-96%.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Pollution | Pollution Control | 13B |
| Coal | Stationary Sources | 08G, 21D |
| Desulfurization | Pyritic Sulfur | 07A, 07D |
| Pyrite | | |
| Chemical Cleaning | | 13H |
| Rinsing | | |
| Extraction | | |

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